

THE KINETIC THEORY

•The M Co. •

APPLICATIONS OF THE KINETIC THEORY

TO GASES, VAPORS, PURE LIQUIDS, AND
THE THEORY OF SOLUTIONS

BY

WILLIAM PINGRY BOYNTON, PH.D.

Assistant Professor of Physics in the University of Oregon



New York:

THE MACMILLAN COMPANY

LONDON: MACMILLAN & CO., LTD.

1904

QC175

B7

QC175
B7

158552

Copyright, 1904

By THE MACMILLAN COMPANY

Set up, electrotyped and printed March, 1904

PREFACE.

This book presupposes a moderate acquaintance with the fundamentals of physics and chemistry, and a mathematical equipment involving familiarity with the differential calculus and at least the notation of the integral calculus. It embodies a course of lectures given at the University of California during the academic years 1898-1901, but includes for the sake of greater completeness of treatment some matter not given in the lectures. For detailed information regarding many of the topics mentioned, as for instance osmotic pressure, and electrolysis, and for a statement of the experimental basis for the theories presented the reader is referred to the standard texts which treat of these topics *in extenso*. The intent in this volume is not so much to discuss these facts and theories by themselves as to present their possible or probable relations to each other in the light of the kinetic theory.

While any adequate treatment of the kinetic theory must be mathematical, and the authoritative treatises put forth by the creators and masters of the theory make severe demands upon the attainments of him who would read them, the theory itself owes its interest and value to the fact that it is fundamentally a physical and not merely a mathematical presentation, that it is not satisfied with coördinating external phenomena by the formulation of geometrical or algebraic laws, but at-

tempts to present to the imagination the mechanism by which things take place. The fact that the behavior of gases, or the laws of dilute solutions, or of electrolysis can be presented by a system of equations which make no mention of molecules, atoms or ions, is no argument for or against their existence. Such a system affords a beautiful example of a mathematical theory, but can never fill the place of a physical theory.

Because it is a physical theory, the kinetic theory must face not only the problems of the gaseous state, but also of the liquid and solid states; not only the problem of pure substances, but also those of mixtures and solutions. To say that it has mastered all these problems is manifestly absurd; yet it seems desirable to present a treatment of as large a part of the field as possible for the sake of symmetry and perspective.

The author entirely disclaims any originality either in material or in the treatment of the subjects considered. His part has been to collect and to attempt a systematic presentation. He has attempted to give credit to the sources of his information, referring to the original papers wherever he has had access to them, or could learn of the original source.

It is a pleasure to acknowledge here my indebtedness to the lectures of Prof. A. G. Webster, and to the section on the kinetic theory by Jaeger, in Winkelmann's "Handbuch der Physik." My wife has given invaluable assistance by copying all the manuscript.

EUGENE, OREGON,

January 19, 1904.

CONTENTS.

CHAPTER I.

INTRODUCTION	I
--------------------	---

CHAPTER II.

IDEAL GASES	7
-------------------	---

Statement of Assumptions, 7. Law of Pressure, 9. Computation of Velocities, 14. Boyle's Law and Temperature Scale, 14. Velocity Lines, 17. Maxwell's Velocity Law, 21. Meaning of a , 26. Average Speed, 28. "Mean Square" Speed, 29. Discussion of Law of Pressure, 31. Mixtures of Gases, 38. Dalton's Law, 39. Temperature, 42. Avogadro's Law, 43. Thermodynamics, 43. First Law, 43. Specific Heats, 44. Adiabatics, 47. Entropy, 51. Second Law, 53. Demon Engine, 54.

CHAPTER III.

GASES WHOSE MOLECULES HAVE DIMENSIONS	55
---	----

Mean Free Path, 55. Relative Speed, 60. Number of Molecules Travelling a Given Distance, 64. Effect on Pressure, 67. Ratio of Specific Heats, 71. Boltzmann's Theorem, 75.

CHAPTER IV.

TRANSPORT PROBLEMS.....	79
-------------------------	----

Conduction of Electricity, 79. Viscosity of Gases, 85. Coefficient of Viscosity, 89. Dependence upon Temperature and Pressure, 91. Conduction of Heat, 92. Correction for Small Pressures, 95. Diffusion,

96. Diffusion into Itself, 98. Collisions in Mixed Gases, 100. Free Path in Mixed Gases, 103. Coefficient of Diffusion, 103. Simplified Coefficient, 105.

CHAPTER V.

CHANGE OF STATE 108

General Phenomena, 108. Water and Steam Lines, 110. Critical Point, 110. Model, 111. Thermodynamics, 112. Thomson's Ideal Isothermal, 117.

CHAPTER VI.

EQUATION OF VAN DER WAALS..... 120

Restrictions removed, 120. Equation of van der Waals, 122. Other Equations, 123. Pressure and Volume Coefficients, 126. Thermodynamics, 128. Formulæ, 132. Ratio of Specific Heats, 134. Form of Isothermals, 135. Critical Point, 138. Corresponding States, 140. Critical Data, 143. Discussion of Critical Volume, 145. Dieterici's Equation, 147. Berthelot's Modification, 150.

CHAPTER VII.

VAPORIZATION 152

Traube's Method, 152. Dieterici's Method, 154. Capable Molecules, 156. Number Passing from Liquid to Vapor, 157. Energy Carried by Them, 158. Momenta, 160. Relations between Speeds and Numbers of Molecules in Liquid and Vapor, 163. Temperature and Speeds, 164. Review of Assumptions, 164. Ratio of Covolumes, 165. Latent Heat, 167. Dieterici's Equation, 171.

CHAPTER VIII.

MOLECULES WITHIN A LIQUID..... 174

Failure of Gas Laws, 174. Mean Free Path, 175. Value of d , 179. Space Occupied by Molecules, 179.

Formula for Pressure, 180. Covolume, 181. Internal Pressure Related to Surface Tension and Coefficient of Compressibility, 182.

CHAPTER IX.

SOLUTIONS..... 185

Mixtures of Gases, 185. Absorption of Gases, 189. Henry's Law, 189. Effect of Temperature, 191. Solution of Liquids, 192. Vapor Over Mixed Liquids, 193. Distillation, 198. Osmosis, 199. Osmotic Pressure, 200. Follows Gas Laws, 202. Relation to Vapor Pressure, 206. Boiling Point, 208. Freezing Point, 209. Raoult's Law, 212. Thermodynamics, 213.

CHAPTER X.

KINETIC THEORY OF SOLUTIONS..... 216

Surface Film, 216. Form of Equation, 217. Partial Pressures, 218. Latent Heat, 219. Heat of Dilution, 222. Osmotic Pressure, 222.

CHAPTER XI.

DISSOCIATION AND CONDENSATION..... 224

Double Decomposition, 224. Dissociation, 224. Boltzmann's Theory of, 225. Alternative Theory, 226. Effect of Density, 231. Resulting Density, 233. Experimental Verification, 236. Polymerization of Water, 237. Electrolytic Dissociation, 238. Ions, 239. Faraday's Laws, 242. Explanation of Electrolysis, 243. Molecular Conductivity, 244. Speed of Ions, 245. Dissociation Constant, 247. Effect of Water, 249. The Galvanic Cell, 250. Solution Pressure, 252. Influence of Solvent, 256. Dissociation of Water, 257. Ionization of Gases, 257. Corpuscles, 259. Condensation Nuclei, 261. Electric Spark, 262. Production and Removal of Corpuscles, 263.

CHAPTER XII.

SUMMARY.....	265
Maxwell's Distribution, 265. H Theorem, 266.	
Entropy and Second Law, 268. Degrees of Freedom,	
268. Escape of Gases from Atmosphere, 270. Law	
of Force between Molecules, 271. Mean Free Path,	
274. Dimensions of Molecules, 276. Thin Films, 277.	
Number of Molecules, 279. Ionic Charge, 280.	
INDEX.....	281



KINETIC THEORY.

CHAPTER I.

INTRODUCTION.

IN the so-called "Kinetic Theory" an attempt is made to explain the inner and invisible relations of matter in a way which shall satisfactorily account for and describe the phenomena which are actually observed.

From the earliest time it has been recognized that there was some relation between heat and motion. The primitive method of obtaining fire by friction between two pieces of wood is evidence of this, and references to the works of writers of the Middle Ages can be given which show the same general idea. The first expression of a fairly clear conception of the ideas which lie at the basis of the Modern Kinetic Theory is probably to be found in Daniel Bernouilli's "Hydrodynamica" which appeared in 1738.

The real foundations of the modern mathematical form of the Kinetic Theory were laid by Joule in 1848, and by Clausius, Maxwell, Boltzmann and others. At first the attempt was made to explain the properties of gases only, a problem which seemed the

more hopeful because of the simple laws which relate the phenomena of gases. Of late years the treatment has been extended with some success to liquids also. We shall attempt to give an elementary treatment of the Kinetic Theory both of liquids and gases.

The object of our treatment is not argumentative, so that for the present it is immaterial whether the theory be regarded as a statement of what actually occurs, or simply as a mechanical analogy, a model, if you please, to help us understand the external phenomena. Yet if the analogy be close enough and extend far enough we hold ourselves free to accept it as more than a simple analogy.

The Kinetic Theory may be regarded as a Special or Specialized Theory of Heat, while Thermodynamics is a more general theory, assuming only that heat is a form of energy, but not describing further the particular form. Hence all the theorems of Thermodynamics must be consistent with the results which we shall obtain, and some of them may appear to derive their validity from causes which we shall unravel.

Certain general notions which belong to the Kinetic Theory may be stated at the outset. Divisibility is ordinarily stated to be one of the properties of matter. Divisibility to an indefinite extent, or infinite divisibility, to use the shorter term, is a purely mathematical conception. Anything which is continuous, as space, or time, can be thought of as infinitely divisible, or divisible at any point indifferently. Physicists and chemists have generally agreed to consider that a sub-

stance may be divided into very small parts without losing its identity as a substance. The smallest parts which can still retain this identity are called *Molecules*. These molecules may be yet further divisible into *Atoms*, which, however, are different in their properties from the molecules which they compose. The atoms themselves are regarded as indivisible. All the molecules of a pure substance are regarded as being just alike in all respects, though the molecules of different substances are different. Similarly all the atoms of one kind are alike in all respects, though there are many kinds of atoms. This theory has been propounded to explain the facts of chemistry, and particularly the fact of combination in definite proportions. We shall find it however a convenient starting point for our work.

We shall think then of a gas as composed of a great number of particles, or molecules, these molecules being for any one gas all just alike, though we may find it convenient sometimes to consider mixtures, in which there will be several sets of molecules of different kinds, but all the molecules of any one kind will be just alike. These molecules will be subject to the laws of mechanics; that is, Newton's laws and their consequences can be applied to them just as to ordinary objects.

If we try to picture to ourselves the behavior and motions of these molecules, we have to imagine them magnified to a very great extent, and then to consider what takes place in a space which is really very

minute. Such a space is represented by Fig. 1. We may think of this, if we choose, as representing the positions of the molecules of a very small portion of a solid. These molecules are to be thought of as all

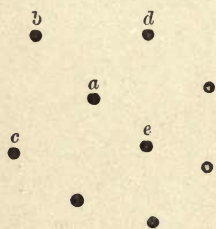


Fig. 1.

in violent motion, but they are subject to mutual attractions, and possibly to repulsions also. It may be that in a solid the molecules occupy a very much larger part of the space than is here represented. It is very probable that they are not sim-

ple in form. But we can think of the points as representing the mean positions of the centers of the molecules. Suppose then that some molecule, as *a*, starts to move to the right. It will be opposed in that motion by the attractions of *b* and *c*, and by *d* and *e*, which it may hit, and rebound, or they may simply exert a repulsive force when *a* gets too near them. Whatever may be the causes, however, *a* soon starts back, swings perhaps past its first position, only to be sent back and to oscillate in some path simple or complex, never getting far from its original position.

If, however, *a*, going to the right manages to escape between *d* and *e*, it may not come back at all to its first place, but may wander now to one part, now to another, of the body. If a great many, or all the molecules have this freedom of motion, we have a picture of the liquid state. In the solid state very little diffusion can take place, but of liquids diffusion

is an especial characteristic, as much so as their mobility.

In the liquid state as we have pictured it, there is still an attractive force between the molecules, that is, liquids exhibit cohesion, and the molecules never get very far apart. In the interior of a liquid this cohesion exhibits no marked effect, except as in connection with the other properties of the molecule it helps determine the density. But near the surface a molecule feels the attraction of the molecules on one side of it, while there are fewer molecules on the other, so that there is an unbalanced tension tending to draw it toward the body of the liquid, or at least to keep it from escaping from the liquid. This unbalanced tension explains why a liquid can have a *free surface*, just as a solid can, and is called *surface tension*.

Most of the molecules of a liquid do not have a sufficiently high velocity when they approach this surface region to enable them to break through and escape from the liquid in spite of the unbalanced attraction, or surface tension; but we shall see later that the molecules do not all have the same velocity, and so some of them which happen to have velocities very much higher than the average may escape through the surface of the liquid into the space above. These molecules will then constitute the vapor of the liquid. If the space above the liquid is confined, after a time some of the free molecules coming back near the surface of the liquid may plunge back into it;

this is condensation, and when the rate at which the molecules are leaving, and the rate at which they return to the liquid, or the rates of evaporation and condensation, are equal, the space above the liquid is said to be *saturated* with the vapor.

CHAPTER II.

IDEAL GASES.

THE volume occupied by a substance in the gaseous state is in general so very much greater than that which it occupies in the solid or liquid state that we are led to believe that the molecules of the gas themselves occupy a very small portion of the space filled by the gas, but that it is by the violent motion of these molecules that the gas can seem to fill all the space.

If we can neglect or disregard the space occupied by the substance of the molecules, we can obtain some quite simple relations. For the sake of simplicity we shall also disregard the effect of gravitation, though we may later ask what its effect may be, and we shall also for the present neglect the effect of the mutual attraction between molecules which in liquids and solids gives rise to cohesion. This we do on the assumption that it is only for a very small portion of the time that a molecule is near enough to any other molecule to be perceptibly affected by its attraction.

Stated more formally, we shall assume that the total volume of the molecules themselves is so small in comparison with the space in which they move that it can be entirely disregarded; that the time during

which two molecules are in contact with each other is very small as compared with the average time during which a molecule is moving between successive impacts, so that in comparison it can be entirely neglected, and so that further there is no probability of the molecules hitting each other in groups of more than two, that is, there will be no collisions of more than two molecules together; and that there are no forces acting upon the molecules except those that arise from and act during collisions.

The molecules will move in straight lines with uniform speed, except when their direction and speed are being changed by a collision. The speeds of different molecules, and the speeds of the same molecule just before and just after a collision may be very different.

For the sake of definiteness in our conceptions and simplicity in our reasoning we shall for the present regard the molecules as smooth, hard, perfectly elastic spheres. Under these assumptions, if we could at any time know exactly the positions and velocities of all the molecules of a gas, it would be only a matter of comparatively simple computations to follow the path of each molecule, to determine its collisions and the velocities resulting from these collisions. But the vast number of the molecules and the frequency of their collisions makes this method of treatment a task of hopeless magnitude.

The other possible method of studying these motions is to confine our attention to some small space,

and study its conditions ; some molecules leave this space, others come in to take their places ; individual molecules change their directions and speeds, but others take the directions and speeds these had. Our study then becomes a matter of statistics, of numbers and averages.

We may however very simply find an answer to the question, what pressure will be exerted by a given body of gas.¹ We shall assume that the body of gas we are studying is confined within a closed receptacle, whose walls may be considered perfectly smooth and hard. Imagine a small portion of one of the walls small enough so that it may be regarded as plane, separated from the rest of the wall so as to be capable of a slight backward and forward motion, as a piston. The continual impact of the molecules of the gas will tend to force this piston back away from the space occupied by the gas, and we shall try to find what force applied to the back of the piston will just suffice to hold it in equilibrium against the impact of the molecules.

On the piston as a base erect an imaginary cylinder of height h , with its walls perpendicular to the piston, and with its opposite base parallel and equal to it. The phenomena inside this cylinder will be exactly the same whether the walls of the cylinder are solid, so that the same molecules rebound and come back into the space, or whether as some go out others come back in to occupy the same space with the same

¹ Joule, *Phil. Mag.* (4), 14, p. 211, 1857.

variety of velocities, just as if they had come from a region which was the exact mirrored image of the region just within the wall. For convenience in computation we shall regard the cylinder as actually existing, with smooth, hard walls, restricting the motions of the molecules.

For convenience we shall also make the two following assumptions, which we know are not in accord with the facts, that all the molecules are moving with the same speed, and that all the molecules are divided equally into three groups, one group consisting of molecules moving perpendicular to the face of the piston, the other two groups having motions parallel to this face, but mutually perpendicular. These two last groups will exert pressure only on the side walls of the cylinder, and we have to consider the effect upon the piston of the first group only, whose motion is perpendicular to it.

Let A = area of face of piston,

h = height of cylinder,

m = mass of one molecule,

n = number of molecules in unit space,

c = common speed of all the molecules.

When one molecule hits the piston, if it were able to just give up all its motion to the piston and itself come to rest, it would exert upon the piston an impulse exactly equal to its momentum, mc ; but the mass of the piston is vastly greater than that of the molecule, and the velocity produced in it is vastly smaller than that of the molecule, hence when the

molecule has just come to rest, if we are to regard it as a smooth, hard sphere, it is in contact with the piston and strongly compressed or distorted; at any rate it is in the very act of rebounding from the piston. Now according to the ordinary laws of reflected motion the molecule will rebound from the piston with the same velocity with which it struck it, and according to Newton's third law, that action and reaction are equal and opposite in direction, there acts upon the piston, still driving it away from the gas, an impulse just equal to the impulse upon the molecule, which gives it again the momentum mc . Hence the total impulse upon the piston due to a single impact of a single molecule is $2mc$.

If the molecule has just hit the piston, before it can hit it again it has to traverse the length of the cylinder h and return, a distance of $2h$ in all, before it hits the piston again; and since it travels a distance c per second, it will be able to hit the piston $c/2h$ times per second. Since the distance c is very large, of the order of one mile in ordinary gases, we do not need to consider the possibility of one more or one less collision per second, depending upon the exact positions of the molecule at the beginning and end of the second. One molecule would then in t seconds hit the piston $c/2h \times t$ times; and the sum of all the impulses given to the piston by the one molecule in the time t is

$$2mc \times \frac{c}{2h} \times t = \frac{mc^2 t}{h}.$$

As yet we have considered only the effect of one molecule; in each unit of volume there are n molecules, and in the whole volume of the cylinder, which is $h \times A$, there must be $n \times hA$ molecules. But not all of these are effective in producing pressure upon the piston, in fact we have expressly assumed that just one third of them, that is, $\frac{1}{3}nhA$, were so effective; consequently the whole impulse upon the piston in the time t will be the product

$$\frac{1}{3}nhA \times \frac{mc^2t}{h} = \frac{1}{3}nmc^2At.$$

To produce equilibrium of the piston this impulse must be opposed by a force which will in the same time have just the same impulse. If we call this force F , we may write

$$Ft = \frac{1}{3}nmc^2At,$$

$$F = \frac{1}{3}nmc^2A.$$

A force F of this amount would on the average be able to hold the piston in position against the repeated blows of the molecules. These blows might seem to cause a slight quivering of the piston, an oscillation back and forth, but the impulse of each blow is so slight and the number so enormous that this oscillation can never be actually observed. Now the force F could be exactly replaced or neutralized by a pressure p upon the piston of such intensity that

$$pA = F.$$

This would give us

$$pA = \frac{1}{3}nmc^2A$$

or

(1)

$$p = \frac{1}{3}nmc^2.$$

The discussion of the validity of the method by which we have derived this equation we shall postpone for a little. For the present we shall assume that it is correct, and see what are its consequences.

It appears immediately that the pressure is proportional to the square of the velocities of the molecules, that is, to their kinetic energy of translation. This conclusion does not depend upon any of the assumptions made, but simply on the two considerations that the impulse of a single impact is proportional to the velocity of the molecule, and the number of the impacts is also proportional to the velocity, and hence the total effect is proportional to the square of the velocity.

We may put the equation in a different form if we consider that since m is the mass of a single molecule and n the number of the molecules in unit volume, the product nm is simply the density of the gas, which we may call ρ . Introducing this we have

$$p = \frac{1}{3}\rho c^2,$$

which may solve for c , getting

$$c^2 = 3p/\rho,$$

$$c = \sqrt{3p/\rho}.$$

This gives us a means of computing the velocity of the molecules of a gas directly from a knowledge of its pressure and density. If we take hydrogen as an example, its density at a pressure of one million dynes per sq. cm. and 0° C. is given as .0000884. This is very nearly atmospheric pressure, the atmosphere being about 1.013 million dynes per sq. cm. These figures give

$$c = \sqrt{\frac{3 \times 1,000,000}{.0000884}}$$

$$= 184,400 \text{ cm. per second.}$$

The formula shows that for other gases at the same pressure or for the same gas at different temperatures but the same pressure the velocity c is inversely as the square root of the density, hence we readily obtain for oxygen $c = 46,100 \text{ cm. per sec.}$,
for nitrogen $c = 49,200 \text{ " " "}$

For any volume v , calling the number of molecules in the space v

$$N = vn,$$

the equation

$$(1) \quad p = \frac{1}{3} nmc^2$$

becomes

$$(2) \quad pv = \frac{1}{3} Nmc^2.$$

This is very much like the equation

$$(3) \quad pv = RT,$$

which describes the behavior of ideal gases. If we regard the two equations as identical, we conclude :

First, that a gas made up as we have described it follows Boyle's or Mariotte's Law.

Second, that such a gas follows the law of Charles, or Gay Lussac, with regard to change of pressure or volume with increasing temperature. That is, a gas made up of an aggregation of small molecules with high velocities, the molecules so small as to occupy only a negligible portion of the space filled by the gas, would exhibit the phenomena of an ideal gas, which actual gases closely approximate.

In coming to this conclusion we have really made one very important assumption, or perhaps better, definition. We have, in stating the identity of the two equations

$$pv = \frac{1}{3}Nmc^2 \qquad pv = RT$$

stated that the temperature of a gas is proportional to the square of the velocity of the molecules of the gas, or to the kinetic energy of the motion of translation of the molecules. This then really defines our temperature scale. We shall for the present accept this definition, and consider all temperatures measured on the scale of a thermometer whose working substance is such an ideal gas. We shall consider this procedure justified if its consequences are consistent with well-ascertained facts.

Before examining further the possible meanings of the equation we shall consider the assumptions we have made as to the velocities of the molecules. That these assumptions should be true is inconceivable. If

the molecules of a gas could be once started to moving in such a way as we have described, in a very small fraction of a second so many collisions would have taken place between the molecules whether of the same set, or of the different sets, that molecules would be moving in every conceivable direction and with almost every conceivable speed. Take for instance such a collision as that represented in Fig. 2.

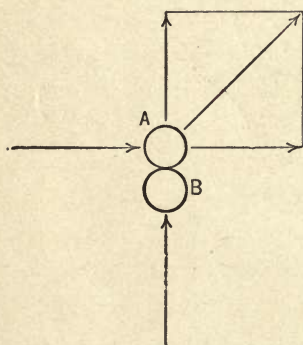


Fig. 2.

The molecules *A* and *B* are moving with equal speeds in directions at right angles to each other, and hit as shown in the figure, so that *B* gives up all its motion to *A*, which had previously no component of its motion in the same direction, but after the collision has a velocity the resultant of the two

previous velocities, and numerically equal to either of them multiplied by $\sqrt{2}$, that is, 1.41. The velocity of *B* in this extreme case is destroyed, while that of *A* is made nearly half as large again. *B* loses all its energy, while, calling the common speed of each before the collision c , the energy of *A* afterward is

$$\frac{1}{2}m(c\sqrt{2})^2 = mc^2,$$

which is just twice its previous energy. This result

was necessary, for the total energy before and after the collision must be the same.

x It is evidently impossible to follow the path of each molecule, and examine the conditions of all its collisions, so the question arises whether there is any other method of studying these actions which will prove fruitful in results. We may perhaps obtain a more definite conception of the problem in the following way ; take any convenient point as the origin of a system of coördinates, and from this point draw a line which shall have the same direction as that of the motion of some particular molecule and a length proportional on some convenient scale to its velocity. We can think of this line or of its end as representing fully the velocity of the molecule. If we consider all the molecules in some small definite space, we may draw for each from this same origin its velocity-line. These velocity-lines will then stick out from this origin in all possible directions, and with a great variety of lengths. We might picture to ourselves the aggregate as an exaggerated spherical hedgehog, with spines infinitely numerous and of every length. We can conceive of no possible reason why the arrangement of the spines or velocity-lines should be different on one side from what it is on any other ; we must expect to find just as many of any one length in one direction as in another.

The arrangement which we are describing is one which may be called in the strictest sense of that term accidental, and is one to which the Theory of

Probabilities may be applied with perfect propriety. For a complete exposition of this theory the reader is referred to more mathematical treatises on the Kinetic Theory, or to text-books on the Method of Least Squares. If we pass any plane through the origin, there will be just the same arrangement on each side of the plane, as if each side were the image of the other mirrored in the plane. If we pass two planes anywhere, parallel to each other, but quite near together, they will contain between them a thin layer or sheet of space which will have a great many of these velocity-lines ending in it. Any two such layers of the same thickness and distance from the origin ought to have just the same number of such lines ending in them.

Suppose that we have drawn the velocity-lines for all the molecules in a unit volume, then there will be just n of these lines. Now, how many of these will end in a particular layer, such as we have described? The number will of course be proportional to n , the total number, and to the thickness of the layer, if that be small. If we call the distance of the nearer side of the layer from the origin u , and its thickness du , we may write the number of these lines

$$nf(u)du.$$

In mathematical terms, this is the number of molecules which have velocities, the X -components of which lie between u and $u + du$.

The factor

$$f(u)du$$

is called the Probability that a molecule should have such a velocity. The function $f(u)$ is a quantity in some way depending upon u , but whose form we do not as yet attempt to assign.

Similarly $nf(v)dv$

is the number of molecules having the Y -components of their velocities between v and $v + dv$, and

$$nf(w)dw$$

the number of those having Z -components between w and $w + dw$; or, $f(v)dv$ and $f(w)dw$ are the respective probabilities that a molecule should have such velocities. We write these functions all in the same form, because we believe the law of probabilities must be the same in every direction.

Now the two planes whose distances from the origin are u and $u + du$ and the two whose distances are v and $v + dv$ intersect to form a little rectangular prism, of infinite length, and of width and thickness du and dv . What is the probability that a molecule has a velocity whose line ends in this prism, that is, in both these layers? By the ordinary theory of probabilities it is the product of the separate probabilities of its ending in either of the two layers, that is it is

$$f(u)f(v)dudv$$

and the probable number of velocity lines ending in the prism is

$$nf(u)f(v)dudv.$$

The third pair of planes cut this prism, forming a little rectangular parallelopiped whose dimensions are du , dv , dw , and by the same process of reasoning, the probability that a velocity-line ends in this little space is

$$f(u)f(v)f(w)dudvdw$$

and the number of them ending in this space is

$$nf(u)f(v)f(w)dudvdw.$$

Now we know two things very definitely about this expression; first that the total number of velocity-lines is n , that is, that the sum or integral of this expression over all space is n , or taking out the common factor n that

$$(4) \quad \int \int \int f(u)f(v)f(w)dudvdw = 1,$$

and second, that the value of the expression, that is, the number of lines ending in the space $dudvdw$ depends only on the size of this space and on its distance from the origin, and not on its direction. Now the distance c is given by the equation

$$c^2 = u^2 + v^2 + w^2;$$

hence we may write

$$f(u)f(v)f(w) = \phi(c^2) = \phi(u^2 + v^2 + w^2)$$

which indicates symbolically the fact we have just stated. We may then write our expression for the number of velocity-lines ending in the space $dudvdw$

$$n\phi(u^2 + v^2 + w^2)dudvdw.$$

It is possible from the facts which we have just stated to derive the forms of the functions f and ϕ , but we shall take the easier method of suggesting the form of solution and testing it to see if it satisfies the conditions which we have stated. Professor J. Clerk Maxwell¹ has suggested the solution

$$(5) \quad f(u) = Ae^{-\frac{u^2}{a^2}}$$

where e is the base of the natural system of logarithms, and A and a are constants to be determined, then

$$\begin{aligned} f(u)f(v)f(w) &= \phi(u^2 + v^2 + w^2) = \phi(c^2) \\ &= A^3 e^{-\frac{u^2 + v^2 + w^2}{a^2}} = A^3 e^{-\frac{c^2}{a^2}}, \end{aligned}$$

and hence satisfies the second of our conditions. The first will be satisfied by giving a proper value to the constant A . Inasmuch as all the molecules of the gas have velocities whose X -components lie between $-\infty$ and $+\infty$, A must have a value which will satisfy the equation

$$\int_{-\infty}^{\infty} nAe^{-\frac{u^2}{a^2}} du = n.$$

This value is found² to be

$$\begin{aligned} A &= \frac{1}{\alpha\sqrt{\pi}} \\ f(u) &= \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{a^2}}, \end{aligned}$$

¹ *Phil. Mag.* (4), 19, p. 22, 1860.

² The equation

$$\int_{-\infty}^{\infty} nAe^{-\frac{u^2}{a^2}} du = n$$

and the number of velocity lines ending in the space $dudvdw$ is

$$\frac{n}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{u^2 + v^2 + w^2}{\alpha^2}} dudvdw$$

We may express these relations graphically by plotting the curve for the equation

$$(6) \quad v = f(u) = \frac{1}{\alpha \sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}},$$

gives

$$A \int_{-\infty}^{\infty} e^{-\frac{u^2}{\alpha^2}} du = 1.$$

The value of a definite integral does not depend upon the particular variable in terms of which the integral is written, hence we may equally well write

$$A \int_{-\infty}^{\infty} e^{-\frac{v^2}{\alpha^2}} dv = 1$$

$$A \int_{-\infty}^{\infty} e^{-\frac{w^2}{\alpha^2}} dw = 1.$$

Multiplying any two of these together, for instance the first two

$$A^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{u^2 + v^2}{\alpha^2}} dudv = 1.$$

We can transform this expression into polar coördinates, r and θ , by writing

$$u^2 + v^2 = r^2$$

and substituting for the infinitesimal area $dudv$ the corresponding expression in polar coördinates, $rdrd\theta$. This gives

$$A^2 \iint e^{-\frac{r^2}{\alpha^2}} r dr d\theta = 1.$$

The integration is to be extended over the whole area of the plane, and this is covered if θ vary from 0 to 2π , and r from 0 to ∞ . Performing the first integration immediately,

which is commonly known as the *Probability Curve*. Its height at any point represents the value of $f(u)$ corresponding to a particular value of u , and if two vertical lines, as AB and CD be drawn at distances from the origin u and $u + du$, the area between them,

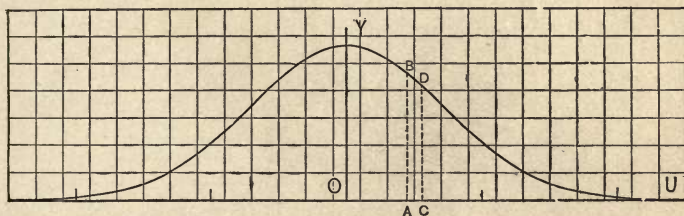


Fig. 3.

having the base du and the height $f(u)$ will represent the number of molecules having the X -component of their velocities between u and $u + du$.

The curve is evidently symmetrical with reference to the axis of Y . It must be so, for positive and negative components are equally numerous. It is

$$2\pi A^2 \int_0^\infty e^{-\frac{r^2}{a^2}} r dr = 1.$$

Now the differential of $e^{-\frac{r^2}{a^2}}$ is

$$e^{-\frac{r^2}{a^2}} \left(-\frac{2r dr}{a^2} \right) = -\frac{2}{a^2} e^{-\frac{r^2}{a^2}} r dr.$$

Hence

$$2\pi A^2 \int_0^\infty e^{-\frac{r^2}{a^2}} r dr = -[\pi A^2 a^2 e^{-\frac{r^2}{a^2}}]_0^\infty = \pi A^2 a^2 = 1,$$

$$A^2 = \frac{1}{\pi a^2},$$

$$A = \frac{1}{a\sqrt{\pi}}.$$

highest in the middle, and it can be proven that this corresponds to the actual distribution of velocities. It is very low at only a short distance, showing that very few molecules have excessively high speeds. The total area between the curve and the horizontal axis is finite, and to correspond to the equation as written must be just equal to unity.

Inasmuch as a great part of our interest is centered upon the speeds of the molecules, and we care comparatively little about their directions since the phenomena are the same in all directions, it is convenient to reduce this expression to a form which does not contain coördinates of direction, like u , v , w , but simply a coördinate of length. Now the finite factors above may be written in the form

$$\frac{n}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{c^2}{\alpha^2}}$$

which contains no reference to direction. The factor $dudvdw$ is simply the volume of the small space in which the velocity-lines under consideration end. We may transform this expression to the corresponding form for polar coördinates, or we may draw our conclusions directly. Consider the thin shell bounded by spherical surfaces of radii c and $c + dc$. All parts of it may be considered as at the same distance c from the origin, and hence as having the same value for the factor

$$\frac{1}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{c^2}{\alpha^2}}.$$

The area of one face of this shell is $4\pi c^2$ and its thickness dc , hence its volume is $4\pi c^2 dc$, and the number of velocity-lines ending in it is

$$\frac{n}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{c^2}{\alpha^2}} \times 4\pi c^2 dc = \frac{4n}{\alpha^3 \sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^2 dc.$$

That is to say, there are this number of molecules which have speeds lying between c and $c + dc$.

The curve whose equation is

$$(7) \quad y = \frac{4}{\alpha^3 \sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^2$$

is shown in Fig. 4. Mathematically, this curve should be symmetrical, positive and negative values of c giving

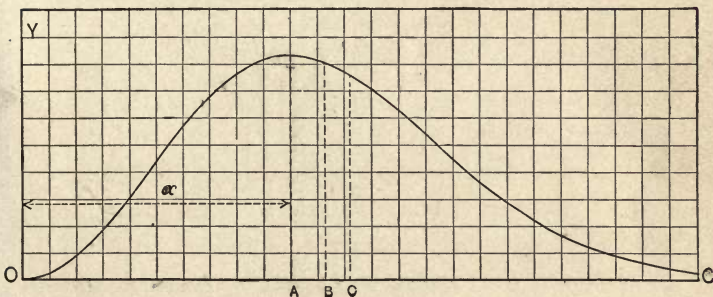


Fig. 4.

ing the same values of y . Physically, we consider only positive speeds, and hence have to consider only the right-hand half of the curve, which is all that is shown in the figure. The general characteristics of the curve are sufficiently shown by the figure, and the interpretation of it is similar to that of Fig. 3. The

highest point of the curve corresponds to the most probable speed and is found by the ordinary method of finding a maximum :

$$\frac{dy}{dc} = \frac{4}{\alpha^3 \sqrt{\pi}} \left[2ce^{-\frac{c^2}{\alpha^2}} - \frac{2c}{\alpha^2} e^{-\frac{c^2}{\alpha^2}} c^2 \right] = 0.$$

Dividing out common factors,

$$1 - \frac{c^2}{\alpha^2} = 0,$$

$$c = \alpha.$$

That is, α is the most probable speed of the molecules. The ordinate, y , for this speed is

$$y = \frac{4}{\alpha^3 \sqrt{\pi}} e^{-\frac{\alpha^2}{\alpha^2}} \alpha^2 = \frac{4}{e\alpha \sqrt{\pi}} = \frac{.832}{\alpha}.$$

That is, the area of a strip of the width $\alpha/10$ at this point is .0832, which is the probability that a molecule will have a speed between $\frac{1}{2}\alpha$ and $\frac{3}{2}\alpha$, or the number of such molecules will be .0832 n , nearly one twelfth of the whole number.

Knowing the number of molecules which have each possible speed, we are able to find several interesting average values. For instance, the average speed of all the molecules is found by multiplying the number of molecules having a certain speed into that speed, doing this for all possible speeds, adding the products so formed, and dividing by the whole number of molecules. This is the ordinary method of taking averages. The analytical expression for this is

$$\frac{1}{n} \int_0^\infty c \times \frac{4n}{\alpha^3 \sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^2 dc = \frac{4}{\alpha^3 \sqrt{\pi}} \int_0^\infty e^{-\frac{c^2}{\alpha^2}} c^3 dc.$$

The integration of this expression¹ is somewhat com-

¹ The integration of expressions of the form

$$\int e^{-x^2} x^n dx$$

may sometimes be helped by the following expedient :

$$d(x^{n-1} e^{-x^2}) = (n-1) x^{n-2} e^{-x^2} dx - 2e^{-x^2} x^n dx;$$

hence transposing, dividing by 2 and integrating,

$$(8) \quad \int e^{-x^2} x^n dx = -\frac{1}{2} x^{n-1} e^{-x^2} + \frac{n-1}{2} \int x^{n-2} e^{-x^2} dx.$$

That is, the integration may be made to depend upon the integration of a form like the original, except that the exponent of x is 2 less than before. Successive applications of this formula will, if n be odd, make the integration depend upon that of

$$(9) \quad \int e^{-x^2} x dx = -\frac{1}{2} e^{-x^2},$$

or if n be even, upon

$$\int e^{-x^2} dx,$$

which is not directly integrable between finite limits, but is easily integrable when the limits are both infinite or zero, by the device used in the last footnote. Calling the integral I ,

$$I = \int_0^\infty e^{-x^2} dx = \int_0^\infty e^{-y^2} dy,$$

$$I^2 = \int_0^\infty \int_0^\infty e^{-(x^2+y^2)} dx dy,$$

or passing to polar coördinates, and making the limits such as to just cover one quadrant,

$$I^2 = \int_0^{\frac{\pi}{2}} \int_0^\infty e^{-r^2} r dr d\theta = \frac{\pi}{2} \int_0^\infty e^{-r^2} r dr,$$

$$= \frac{\pi}{4} [-e^{-r^2}]_0^\infty = \frac{\pi}{4},$$

$$I = \frac{1}{2} \sqrt{\pi}.$$

plicated, being accomplished by what is commonly termed integration by parts. We give here the result, indicating the fact that it is an average value by a line drawn over the \bar{c} .

$$(10) \quad \bar{c} = \frac{2a}{\sqrt{\pi}}.$$

This method of obtaining averages is perfectly general and we may apply it to other powers of the speed, by treating them as we have c ; for instance, the average value of the square of the speed is

Using these devices, the mean speed is

$$\frac{4}{a^3\sqrt{\pi}} \int_0^\infty e^{-\frac{c^2}{a^2}} c^3 dc,$$

which becomes, letting $c/a = x$

$$\begin{aligned} \frac{4a}{\sqrt{\pi}} \int_0^\infty e^{-x^2} x^3 dx &= \frac{4a}{\sqrt{\pi}} \left[-\frac{1}{2} x^2 e^{-x^2} \right]_0^\infty + \frac{4a}{\sqrt{\pi}} \times \frac{2}{2} \int_0^\infty x e^{-x^2} dx, \\ &= \frac{4a}{\sqrt{\pi}} \left[-\frac{1}{2} e^{-x^2} \right]_0^\infty = \frac{2a}{\sqrt{\pi}}, \end{aligned}$$

since $x^2 e^{-x^2}$ vanishes at both the limits 0 and ∞ .

Similarly the mean square of the speed is

$$\begin{aligned} \frac{4}{a^3\sqrt{\pi}} \int_0^\infty e^{-\frac{c^2}{a^2}} c^4 dc &= \frac{4a^2}{\sqrt{\pi}} \int_0^\infty e^{-x^2} x^4 dx, \\ &= \frac{4a^2}{\sqrt{\pi}} \left[-\frac{1}{2} x^3 e^{-x^2} \right]_0^\infty + \frac{4a^2}{\sqrt{\pi}} \times \frac{3}{2} \int_0^\infty e^{-x^2} x^2 dx \\ &= \frac{4a^2}{\sqrt{\pi}} \times \frac{3}{2} \left[-\frac{1}{2} x e^{-x^2} \right]_0^\infty \\ &\quad + \frac{4a^2}{\sqrt{\pi}} \times \frac{3}{2} \times \frac{1}{2} \int_0^\infty e^{-x^2} dx \\ &= \frac{4a^2}{\sqrt{\pi}} \times \frac{3}{2} \times \frac{1}{2} \times \frac{1}{2} \sqrt{\pi} = \frac{3}{2} a^2, \end{aligned}$$

the expressions $x^3 e^{-x^2}$ and $x e^{-x^2}$ vanishing at both the lower and upper limits.

$$\begin{aligned}
 \overline{c^2} &= \frac{1}{n} \int_0^\infty c^2 \times \frac{4n}{\alpha^3 \sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^2 dc \\
 (11) \qquad &= \frac{4}{\alpha^3 \sqrt{\pi}} \int_0^\infty e^{-\frac{c^2}{\alpha^2}} c^4 dc = \frac{3\alpha^2}{2}.
 \end{aligned}$$

We might similarly find the average values of c^3 , c^4 , etc., but the values which we have deduced are the only ones of practical importance.

We can readily compare the relative magnitudes of the different speeds. The most probable speed was α , its square α^2 . The average speed is somewhat larger, being $2\alpha/\sqrt{\pi}$, its square $4\alpha^2/\pi$. The average of the square of the speed, commonly spoken of as the "mean square" of the speed, is $3\alpha^2/2$.

These three squares then are in the ratios of

$$1 : 1.27 : 1.5$$

or the speeds themselves in the ratios

$$1 : 1.128 : 1.225$$

the most probable speed being the least, the square root of the "mean square" the greatest. They are represented in Fig. 4 by the distances OA , OB , OC , respectively. The corresponding values of

$$(7) \qquad y = \frac{4}{\alpha^3 \sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^2$$

are found to be

$$\frac{.832}{\alpha}, \quad \frac{.805}{\alpha}, \quad \frac{.755}{\alpha}.$$

That is, the number of molecules having speeds not differing more than $1/20\alpha$ either way from the three speeds are $.0832n$, $.0805n$, $.0755n$, respectively, or about $1/12$, $1/12.4$, $1/13.25$ of the whole number of molecules.

The reason why these average speeds are greater than the "most probable speed," is not so much that the higher speeds are more numerous as simply that the higher speeds contribute so much more to the sum of the products, and hence exert a preponderating influence. We can, if necessary, find the number of molecules whose speed does not exceed a given value c , by evaluating the integral

$$\frac{4}{\alpha^3 \sqrt{\pi}} \int_0^c e^{-\frac{c^2}{\alpha^2}} c^2 dc$$

but this involves very difficult and indirect methods,¹

¹ The integration of the expression

$$\frac{4}{\alpha^3 \sqrt{\pi}} \int_0^c e^{-\frac{c^2}{\alpha^2}} c^2 dc$$

depends upon the integration between finite limits of

$$\int e^{-x^2} x^2 dx,$$

which again depends (see last footnote) on

$$\int e^{-x^2} dx.$$

For small values of x this may be evaluated by substituting for e^{-x^2} the series

$$e^{-x^2} = 1 - x^2 + \frac{x^4}{2} - \frac{x^6}{3} +, \text{ etc.}$$

Then

$$(12) \quad \int e^{-x^2} dx = \int dx - \int x^2 dx + \frac{1}{2} \int x^4 dx - \frac{1}{3} \int x^6 dx + \dots$$

and is perhaps easiest done by plotting the curve of Fig. 4 very carefully and measuring the area between it and the horizontal axis to the left of the ordinate c . It can be shown that .4276 of all the molecules have speeds not exceeding α , the most probable speed; .5331 of them have speeds not exceeding $2\alpha/\sqrt{\pi}$, the average speed; .6082 do not exceed $\sqrt{\frac{3}{2}}\alpha$, the "mean square" speed; while for 1.5, 2, and 2.5 times α , the proportions are .7877, .9540, .9940, respectively. It can be shown that not more than one in 12.5×10^9 have speeds over 5α , and less than one in 236×10^{40} over 10α . From a study of these numbers one sees what is shown by simple inspection of the curve, that the great majority of these molecules have speeds not much less, nor very much greater than these probable or average speeds which we have been discussing.

✕ We have previously attempted a computation of the pressure exerted by a perfect gas upon the walls

For large values of x we may write

$$\begin{aligned}\int_0^x e^{-x^2} dx &= \int_0^\infty e^{-x^2} dx - \int_x^\infty e^{-x^2} dx \\ &= \frac{1}{2}\sqrt{\pi} - \int_x^\infty e^{-x^2} dx,\end{aligned}$$

and the integration of this last term may be effected by successive applications of the formula developed in the last note,

$$\int e^{-x^2} x^n dx = -\frac{1}{2} x^{n-1} e^{-x^2} + \frac{n-1}{2} \int x^{n-2} e^{-x^2} dx,$$

giving

$$(13) \quad \int_x^\infty e^{-x^2} dx = e^{-x^2} \left(\frac{1}{2x} - \frac{1}{4x^3} + \frac{3}{8x^5} - \frac{15}{16x^7} + \dots \right).$$

By the use of one or the other of these two formulæ the numbers given in the text can be calculated.

of the containing vessel. For convenience in effecting the computation we made several assumptions which we acknowledge frankly were not in accordance with the probable facts. In particular, we assumed that all the molecules had the same speeds, and that all were moving in one or the other of three mutually perpendicular directions. Now while such an arrangement might possibly exist for an instant of time, it is very improbable, and could not be permanent. The distribution of speeds and directions which we have been studying can be shown to be the most probable, and to be capable of permanence. Assuming then that the molecules have such velocities, how will the formula

$$(1) \quad p = \frac{1}{3} n m c^2$$

be affected? Which of the various speeds we have studied is to be understood as the c of this equation? Granted that our reasoning which leads to the general form of this equation is right, have we the right constant factor? Let us repeat the deduction in the light of our study of the difference of velocities. Suppose the gas to be confined between two plane parallel walls as before. Laterally it makes no difference whether it is bounded by a cylindrical surface as before, or whether the parallel walls extend to an indefinite distance. We shall take our system of coördinates such that the axis of X is perpendicular to these walls. The speed of any molecule we shall call c , and the angle between the direction of its motion and

the X axis θ . The component of its velocity perpendicular to the two planes we can then call either $c \cos \theta$ or u . The other component, $c \sin \theta$, parallel to the planes, will not be affected at all by the impact with the planes, and so does not have to be taken into account. We shall as before entirely disregard the mutual collisions of the molecules, because, while these change the velocities of individual molecules, on the average they leave the distribution the same, that is, we assume that our gas is in a steady state. If as before we call the distance between the two planes h , a molecule will travel between two successive impacts against the same plane a distance of $2h$ in the direction perpendicular to the plane, or an actual distance $2h/\cos \theta$. It will hit the plane then $(c \cos \theta)/2h$ or $u/2h$ times per second. The impulse given the plane by a single impact of a single molecule will be, by the same reasoning as before, $2mc \cos \theta$, or $2mu$. The total impulse from a single molecule in a second will then be the product of these, namely

$$(14) \quad \frac{mc^2 \cos^2 \theta}{h} \text{ or } \frac{mu^2}{h}.^1$$

¹ The two deductions of the equation of pressure given in the text are not the only ones possible. Some forms of the demonstration depend upon considerations involving a knowledge of the space occupied by the molecules. Others depend directly upon abstruse but general theorems in dynamics. The demonstration in the text can be completed in the following manner, which is more analytical in its form, but not more rigid. We will take into consideration a large surface, of area s , so large that we can neglect the number of molecules which pass in and out of the bounding cylindrical surface. The volume we are consider-

If we imagine a right prism having bases of unit area in the two parallel planes, its volume will be numerically equal to its height, h , and the total number of molecules in it will be $n h$. Not all these will be moving in such directions as to hit the plane surface we are considering within the base of the prism, but on the average among the myriads of molecules as many will come into the space as go out, and with

ing is $h s$, and the total number of molecules in this volume is $n h s$. The sum of all the impulses in one second due to a single molecule of speed c the direction of whose motion makes an angle θ with the axis of X is

$$\frac{m c^2 \cos^2 \theta}{h}.$$

The number of molecules making this angle θ with the axis of X can be found as follows. In the accompanying figure let OX represent the di-

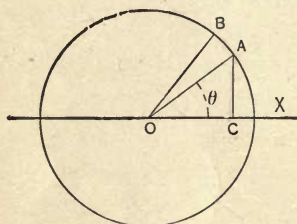


Fig 5.

rection of the axis of X , and let the angle $AOX = \theta$. All the velocity lines drawn from O whose inclinations to OX lies between θ and $\theta + d\theta$ will be comprised between the two conical surfaces generated by the rotation of OA and OB about OX as an axis, and the number of them will be proportional to the solid angle subtended by the zone generated

by the arc AB . Now letting $OA = r$ the area of this zone is

$$2\pi AC \times AB = 2\pi r \sin \theta r d\theta = 2\pi r^2 \sin \theta d\theta.$$

The whole area of the spherical surface described in this rotation is $4\pi r^2$ but since we are concerned only with the direction of the line, and not with the direction of motion along that line, all possible directions are included by the lines piercing one half the spherical surface, whose area is $2\pi r^2$. The ratio of these two areas then is

$$(15) \quad \frac{2\pi r^2 \sin \theta d\theta}{2\pi r^2} = \sin \theta d\theta,$$

similar velocities, so that while not all the identical molecules which are at any one time within this prism strike its base, yet the total number available for striking this base is the same, namely n/h . Then the total impulse on the base due to all the molecules is the sum of all the impulses of all the molecules, or

$$\sum_1^{nh} \frac{mv^2}{h}.$$

We may take m/h outside the sign of summation, and remembering that

$$\frac{1}{h} \sum_1^{nh} = \sum_1^n,$$

which gives the relative number of molecules having the inclination of their paths to the axis of X between θ and $\theta + d\theta$. The total number of such molecules will be then

$$nhs \sin \theta d\theta.$$

The number of these having speeds between c and $c + dc$ could be expressed according to the formulæ which we have discussed, but we can obtain directly the results of integrating these formulæ by writing for c^2 its average value \bar{c}^2 , which gives us for the impulse arising from the impacts upon the surface of all the molecules whose directions lie between the limits stated

$$\begin{aligned} nhs \sin \theta d\theta \times \frac{m\bar{c}^2 \cos^2 \theta}{h} \\ = nsm\bar{c}^2 \cos^2 \theta \sin \theta d\theta, \end{aligned}$$

and the force which must be applied to maintain equilibrium is

$$F = ps = nsm\bar{c}^2 \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta,$$

$$p = nm\bar{c}^2 \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta = nm\bar{c}^2 \left[-\frac{\cos^3 \theta}{3} \right]_0^{\pi/2} = \frac{1}{3} nm\bar{c}^2$$

which is the same as the result obtained in the text.

the expression for the total impulse becomes

$$m \sum_1^n u^2.$$

This being the total impulse exerted in one second upon unit area, is numerically equal to the pressure which would hold it in equilibrium. Now

$$\sum_1^n u^2$$

can be represented by $n\bar{u}^2$, that is, n times the average of the square of u , this being simply the definition of the average; hence our expression becomes

$$p = nm\bar{u}^2.$$

Now $c^2 = u^2 + v^2 + w^2$, and summing for all the molecules

$$\sum_1^n c^2 = \sum_1^n u^2 + \sum_1^n v^2 + \sum_1^n w^2$$

$$n\bar{c}^2 = n\bar{u}^2 + n\bar{v}^2 + n\bar{w}^2$$

$$\bar{c}^2 = \bar{u}^2 + \bar{v}^2 + \bar{w}^2.$$

But we have assumed that there is no intrinsic difference in direction in the gas, hence we are compelled to write

$$\bar{u}^2 = \bar{v}^2 = \bar{w}^2;$$

hence

$$\bar{u}^2 = \frac{1}{3}\bar{c}^2$$

and

$$p = nm\bar{u}^2 = \frac{1}{3}nm\bar{c}^2.$$

This expression is identical with that obtained by the previous method, and hence we wish to find why

it is that our faulty assumptions there led to a correct result. It is evident that the c^2 of that formula is what we now recognize as the "mean square" of the velocity. The method of the deduction of the impulse due to the successive impacts of a single molecule shows that it is proportional to the kinetic energy associated with the component of its motion perpendicular to the plane against which the pressure is exerted. Considerations of symmetry lead us to believe that whatever may be the motions of the individual molecules, the total kinetic energy of translation of the molecules of the gas is equally distributed between the three components of the motion, that is, if we write

$$\sum_1^n \frac{1}{2} mc^2 = \sum_1^n \frac{1}{2} mu^2 + \sum_1^n \frac{1}{2} mv^2 + \sum_1^n \frac{1}{2} mw^2,$$

$$\sum_1^n \frac{1}{2} mu^2 = \sum_1^n \frac{1}{2} mv^2 = \sum_1^n \frac{1}{2} mw^2 = \frac{1}{3} \sum_1^n \frac{1}{2} mc^2.$$

This relation, that the kinetic energies associated with the three components of the motions of translation of the particles were equal to each other, and each equal to one third the total energy of translation of all the molecules, was expressly stated in the last deduction. In the first, the assumption that all the molecules had the same speed, and that one third the number were moving in a direction parallel to each of the three principal axes made a correct distribution of the energy, although in a manner entirely arbitrary. But since the result obtained depended only on the distribution of the energy, and not upon the device by

which this was accomplished, the results obtained were trustworthy.

So far we have restricted ourselves to a study of the behavior of a gas all of whose molecules were exactly alike; now we shall ask what is the behavior of a mixture of different kinds of gases. We shall assume that we have in the space that we are considering several classes of molecules, which we shall distinguish by the subscripts 1, 2, etc. Then in unit volume the numbers of molecules of each kind will be n_1, n_2, \dots respectively; the masses of single molecules m_1, m_2 , etc. Now from our last deduction of the pressure exerted by a gas on a plane surface, it appears that

$$p = \frac{1}{3} \sum_1^n mc^2,$$

and the deduction of the formula in this form does not depend upon any assumption as to the uniformity of either the masses or speeds of the molecules; hence if there are several sorts, provided in each sort there is a thorough distribution of the velocities, if

$$n = n_1 + n_2 + n_3 + \text{etc.}$$

we may write

$$\begin{aligned} p &= \frac{1}{3} \sum_1^{n_1} m_1 c_1^2 + \frac{1}{3} \sum_1^{n_2} m_2 c_2^2 + \frac{1}{3} \sum_1^{n_3} m_3 c_3^2 + \text{etc.} \\ &= p_1 + p_2 + p_3 + \text{etc.} \end{aligned}$$

That is, *the total* pressure exerted by a mixture of several gases upon the walls of the receptacle contain-

ing them is the sum of the separate pressures which each would exert if it were occupying the same space *alone*. This is often called DALTON'S LAW.

We next wish to find the result of the mutual collisions between molecules of two different kinds.

If we draw the line joining the centers of the two colliding molecules just at the instant of collision, the mutual forces of the collision will act along this line, and the components of the velocities of the molecules in this direction will suffer change, while the components perpendicular to this direction will not be changed, and will not need to be taken into account. Since the molecules are perfectly elastic, we have not simply the sum of the momenta of the two molecules along this line the same after impact as before, but also the sum of the kinetic energies of translation of the two molecules will remain constant, none of it having the opportunity to degenerate into motion of smaller parts. If we represent these component velocities by p_1 and p_2 before the collision and P_1 and P_2 after it, we have for a single collision

$$m_1 p_1 + m_2 p_2 = m_1 P_1 + m_2 P_2,$$

$$\frac{1}{2} m_1 p_1^2 + \frac{1}{2} m_2 p_2^2 = \frac{1}{2} m_1 P_1^2 + \frac{1}{2} m_2 P_2^2,$$

which are sufficient to determine P_1 and P_2 . From the first equation we get

$$P_1 = p_1 + \frac{m_2}{m_1} (p_2 - P_2).$$

Substituting this in the second and solving for P_2 we get

$$P_2 = \frac{2m_1 p_1 + (m_2 - m_1)p_2}{m_1 + m_2} \quad \text{or} \quad p_2$$

and hence

$$P_1 = \frac{2m_2 p_2 + (m_1 - m_2)p_1}{m_1 + m_2} \quad \text{or} \quad p_1.$$

The second pair of values indicates simply that the equations are satisfied if the molecules neither of them change their motion; but this case we are expressly excluding from our consideration, hence the first pair of values is that in which we are interested. Using these, we find that the difference of the kinetic energies of the two molecules after the collision is

$$\begin{aligned} \frac{1}{2}m_1 P_1^2 - \frac{1}{2}m_2 P_2^2 = & \left[\frac{8m_1 m_2}{(m_1 + m_2)^2} - 1 \right] \left(\frac{1}{2}m_2 p_2^2 \right. \\ & \left. - \frac{1}{2}m_1 p_1^2 \right) + \frac{4m_1 m_2 (m_1 - m_2) p_1 p_2}{(m_1 + m_2)^2}. \end{aligned}$$

Now this equation applies simply to a single collision of a single pair of molecules. In the case of such a mixture as we are considering there will be an exceedingly large number of such collisions and what we are interested in most is the sum total of effect, or the average effect. It does not appear from the above expression whether the difference in the kinetic energies of the two molecules is increased or decreased. With regard to the effect upon the gases in general, we can arrive at more definite conclusions.

The second term of the second member of the equation will be the same for every collision of the sort we are considering except for the factor $p_1 p_2$. If we con-

sider all the cases in which p_1 and p_2 have given magnitudes, we believe that there will be just as many cases where they have the same signs as where they have the opposite signs; hence adding all these together, all the terms of this form will cancel each other, and we need only to consider the effect of the first term.

The second factor of the first term is simply the difference of the energies of the molecules before the collision, hence we conclude that the average difference of their energies after their collision is greater or less than the average difference before, according as the absolute value of the factor

$$\frac{8m_1m_2}{(m_1 + m_2)^2} - 1$$

is greater or less than unity. The expression is perfectly symmetrical with regard to m_1 and m_2 . Assuming that

$$\frac{8m_1m_2}{(m_1 + m_2)^2} - 1 < 1,$$

this expression may be reduced to

$$\frac{4m_1m_2}{(m_1 + m_2)^2} < 1,$$

$$4m_1m_2 < m_1^2 + m_2^2 + 2m_1m_2,$$

$$0 < m_1^2 + m_2^2 - 2m_1m_2,$$

$$0 < (m_1 - m_2)^2,$$

which is true unless

$$m_1 = m_2;$$

hence the factor

$$\frac{8m_1m_2}{(m_1 + m_2)^2} - 1$$

is less than unity whether m_1 or m_2 be greater, and *the difference between the average kinetic energies of the two sets of molecules tends to decrease with every collision.* This very important theorem is due to Professor J. Clerk Maxwell.¹ We conclude from it that when a mixture of gases is in equilibrium, the average kinetic energies of each of the kinds of molecules will be the same.

Now we know that the physical result of intimate contact and mixture is equality of temperature, and we have previously been led to believe that the temperature of a single gas is proportional to the mean square of the velocity of its molecules, or to their mean kinetic energy, hence we state :

Two gases are at the same temperature when their molecules have the same mean kinetic energy ; and the temperature of a gas is proportional to the mean kinetic energy of translation of its molecules.

If different gases are at the same temperature and pressure, we may write

$$p = \frac{1}{3}n_1m_1\overline{c_1^2} = \frac{1}{3}n_2m_2\overline{c_2^2} = \frac{1}{3}n_3m_3\overline{c_3^2} = \dots$$

and

$$\frac{1}{2}m_1\overline{c_1^2} = \frac{1}{2}m_2\overline{c_2^2} = \frac{1}{2}m_3\overline{c_3^2} = \dots,$$

¹ *Phil. Mag.* (4), 19, p. 25, 1860.

from which we conclude that

$$n_1 = n_2 = n_3 = \dots,$$

or, *equal volumes of different gases under the same pressure and at the same temperature contain the same number of molecules.* This result is known as AVOGADRO'S LAW and has been reached independently from purely physical and chemical considerations.

Thermodynamics of an Ideal Gas.—The laws of thermodynamics are deduced in a manner which is entirely independent of any assumptions as to the exact mechanism of that form of energy which we call heat, but can evidently be used equally well for the study of heat phenomena in cases where the mechanism is explicitly stated. The principle of the conservation of energy is often called the first law of thermodynamics and stated as follows :

If any quantity of heat is given to an object or a system of objects, the sum of its total effects in increasing the internal energy and in causing the system to do work against external forces is proportional, or if measured in proper units, equal to the amount of heat so given. This law is often briefly expressed symbolically by the equation

$$dQ = dU + dW,$$

where dQ represents the heat given to the substance, dU the increase of its intrinsic energy, and dW the external work done by it. As the external work often consists in increasing the volume of the substance

against external pressure, the term dW is often replaced by $p dv$, giving us the less general form

$$dQ = dU + p dv.$$

In the case of such an ideal gas as we have just been considering the energy of a definite amount, containing N molecule, is evidently $\frac{1}{2} N m \bar{c}^2$, and further, since we have seen that the temperature is proportional to the energy, we may write this $U = \frac{1}{2} N m \bar{c}^2 = CT$ where C is some constant. The first law then becomes for such a gas

$$dQ = C dT + p dv.$$

It appears immediately from this equation that this constant C is the amount of heat required to increase the temperature one degree when the volume is kept constant, or the specific heat at constant volume, hence we will indicate this by the subscript v , and write

$$(16) \quad dQ = C_v dT + p dv.$$

This will be recognized as a familiar form of the first law as applied to ideal gases. From the statements which we have previously made, that the temperature is proportional to the mean kinetic energy of the molecules, it follows immediately that increasing the volume of the gas without changing its temperature does not change its energy, that is, that $\partial U / \partial v = 0$. This result which follows immediately from the kinetic theory, has been found by very careful experiments to hold true for actual gases just in proportion

as they conform to the equation of ideal gases, $p v = R T$, or may be deduced for gases conforming to this equation by means of the second law, which will be referred to later.

If, on the other hand, the gas be allowed to expand, but kept under constant pressure, the external work will be

$$p(v_2 - v_1) = p v_2 - p v_1.$$

If the equation of the gas be written

$$(2) \quad p v = \frac{1}{3} N m \overline{c^2}$$

this becomes

$$\begin{aligned} p v_2 - p v_1 &= \frac{1}{3} N m \overline{c_2^2} - \frac{1}{3} N m \overline{c_1^2} \\ &= \frac{1}{3} N m (\overline{c_2^2} - \overline{c_1^2}). \end{aligned}$$

The increase in intrinsic energy in increasing the speeds by the same amount will be

$$\frac{1}{2} N m \overline{c_2^2} - \frac{1}{2} N m \overline{c_1^2} = \frac{1}{2} N m (\overline{c_2^2} - \overline{c_1^2}).$$

This last is the energy absorbed in heating the gas at constant volume simply, while the sum of the two, $\frac{5}{6} N m (\overline{c_2^2} - \overline{c_1^2})$, is the amount absorbed in heating it at constant pressure. Hence if we designate the specific heat at constant pressure by C_p , we have the relation

$$\frac{C_p}{C_v} = \frac{\frac{5}{6} N m (\overline{c_2^2} - \overline{c_1^2})}{\frac{1}{2} N m (\overline{c_2^2} - \overline{c_1^2})} = \frac{5}{3} = 1.6.$$

This "ratio of the two specific heats" is a quantity which can be determined directly by experiment, and

is found to have different values for different gases, but for none to exceed this value. The causes of variation will be discussed later, but evidently such an ideal gas as we have been studying is to be considered as monatomic, and for mercury vapor, which is on account of its density regarded as monatomic, the value of this ratio is found to be 1.666.

By comparison with the equation

$$(3) \quad pv = RT$$

it can be easily shown that

$$(17) \quad C_p = C_v + R$$

and that the first law may be written in the other two forms

$$(18) \quad dQ = C_p dT - v dp,$$

$$(19) \quad dQ = \frac{C_p}{R} p dv + \frac{C_v}{R} v dp.$$

Incidentally since

$$C_v = \frac{\frac{1}{2} N m \bar{c}^2}{T}$$

and since for different gases at the same temperature the mean kinetic energy of the molecules is the same,

$$\frac{C_v}{N} = \frac{\frac{1}{2} \bar{m} \bar{c}^2}{T},$$

is independent of the kind of molecule, or otherwise stated, *The specific heat of the molecule is the same for all gases*; or, otherwise, the specific heats of gases are inversely as their molecular weights, or yet again,

equal volumes of gases have equal capacities for heat. This conclusion is to be taken subject to the limitations which we have just stated, namely, that it is based upon assumptions which only apply to especially simple monatomic gases.

In treatises on thermodynamics it is shown that dQ is not a perfect differential, that is, mathematically speaking, if two different states of a gas are designated by the indices 1 and 2, $\int_1^2 dQ$ may have very different values, according to the manner in which the gas is made to pass from the state 1 to the state 2. Physically, the amount of heat the gas will absorb in passing from the state 1 to the state 2 depends upon the manner in which it is made so to pass. We apply to such a passage from one state to another the term *Transformation*. There are two particularly important types of transformations which are called reversible, the *isothermal* transformation, in which the temperature of the body is kept constant, and the *adiabatic* transformation in which no heat is allowed to enter or leave a body. Any series of transformations at the end of which a body is in exactly the same condition in which it was at the beginning of the series is called a *Cycle*. A reversible cycle is one made up entirely of reversible transformations. The simplest reversible cycle is *Carnot's* reversible cycle, which is made up of two isothermal and two adiabatic transformations.

In the accompanying diagram if we represent the volume of a given body of gas by the abscissa, and its

pressure by the ordinate of a point, since these two also determine its temperature, we can regard the point as determining or representing completely the state of the body. A transformation will be represented on this diagram by a line, one in which the

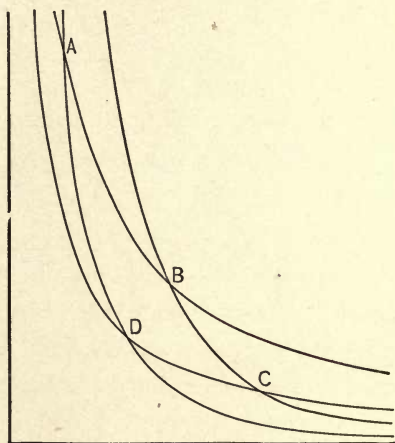


Fig. 6.

pressure is kept constant by a horizontal line, if the volume is kept constant by a vertical line, or if the temperature is kept constant by the curve whose equation is Boyle's Law, $pv = \text{const.}$, that is, an equilateral hyperbola, with the axes as asymptotes. To find the equation of an adiabatic transformation we may take any of the forms of the first law, but will select the one containing the two coördinates p and v ,

$$(19) \quad dQ = \frac{C_p}{R} p dv + \frac{C_v}{R} v dp.$$

The definition of an adiabatic transformation is that no heat is allowed to enter or leave the substance, that is

$$dQ = 0.$$

Hence

$$\frac{C_p}{R} p dv + \frac{C_v}{R} v dp = 0,$$

$$\frac{C_p}{C_v} \frac{dv}{v} + \frac{dp}{p} = 0,$$

$$\frac{C_p}{C_v} \log v + \log p = \text{const.},$$

or

$$(20) \quad p v^{\frac{C_p}{C_v}} = \text{const.}$$

These adiabatic curves are very much like the isothermals, except that they are everywhere steeper. In Fig. 6 $ABCD$ represents a Carnot's Cycle, of which AB and DC represent isothermal and AD and BC adiabatic transformations. Suppose the gas to be brought from the state A to the state C first by the transformations AB and BC , and then by the transformations AD and DC . The amount of heat absorbed in the first transformation is

$$\int_A^B dQ = \int_A^B C_v dT + \int_A^B p dv,$$

in which, since the temperature is constant, dT , and hence

$$\int_A^B C_v dT$$

vanishes, and the amount of heat required is equal to the amount of work done, that is

$$Q_{AB} = \int_A^B p dv = \int_A^B \frac{RT}{v} dv = RT_A [\log v]_A^B$$

Q_{BC} is explicitly stated to be zero, since BC is an adiabatic transformation. Similarly in the transformation ADC

$$Q_{AD} = 0$$

and

$$Q_{DC} = RT_D [\log v]_D^C.$$

These two quantities of heat are not equal, and by algebraic substitutions it is easy to show that the amount of work done in the adiabatic transformations BC and AD is the same, and hence the difference between Q_{AB} and Q_{DC} is equal to the difference between the amounts of work done by the gas in the two transformations, or to the area enclosed by the figure $ABCD$. But according to the theory of differential equations there should be an integrating factor for the equation, and $1/T$ is such a factor, for multiplying both members of the equation

$$dQ = C_v dT + p dv$$

by $1/T$, and remembering that $p = RT/v$ we have

$$\frac{dQ}{T} = C_v \frac{dT}{T} + R \frac{dv}{v},$$

of which the second member is an exact differential, of the quantity

$$C_v \log T + R \log v.$$

We may therefore write

$$\frac{dQ}{T} = dS,$$

$$(21) \quad S = C_v \log T + R \log v + \text{const.}$$

Now this quantity S , which we here meet simply as a quantity which satisfies a certain differential equation, is called the *entropy* of the gas. We may get a physical conception of its meaning in the following manner :

The condition for an adiabatic transformation is

$$dQ = 0,$$

if this be true then

$$dS = 0,$$

and in an adiabatic transformation the entropy of the gas is not changed, or in other words, the transformation is *isentropic*. Hence we can think of the entropy of a substance as the property which is not changed when the substance is compressed or expanded without allowing heat to enter or leave it.

The differential equation for the entropy

$$TdS = dQ$$

gives us, by analogy with the equation,

$$p dv = dW,$$

a suggestion as to its nature. In both equations the right-hand side represents energy, the first in the form of heat, the second in the form of work against external forces. The left-hand side is of the same

form in both equations, consisting of what may be called an *intensity* factor, T or p , and a *quantity* factor, dS , or dv , the differential of the coördinate in which change is experienced. Entropy is then a *quantity* factor rather than an *intensity* factor, and bears the same relation to *temperature* and *heat* which the *volume* of a substance does to its *pressure* and *work*. We do not know the dimensions of either temperature or entropy, but only those of their product, heat. In this respect they are like the electrical units, whose dimensions are made apparently definite only by perfectly arbitrary, although convenient, assumptions.

Other expressions for the entropy may be deduced either by substituting the values of v or T from the equation, or directly.

The form which we have deduced

$$(21) \quad S = C_v \log T + R \log v + \text{const.}$$

easily reduces to the form

$$(22) \quad S = R \log (T^{\frac{C_v}{R}} v) + \text{const.}$$

which for the monatomic gases we have been studying takes the simple form

$$S = R \log (T^{\frac{3}{2}} v) + \text{const.}$$

The equation

$$dQ = TdS$$

or the special form for a reversible cycle

$$\oint \frac{dQ}{T} = 0,$$

which means that the integral of the function dQ/T taken completely about such a cycle vanishes, or in other words that the entropy, of which dQ/T is the exact differential, depends only upon the state of the substance, and not on its history, is a mathematical statement of the Second Law of Thermodynamics. The particularly simple form of these equations depends upon our happy choice of a thermometer scale, and hence upon the properties of the ideal gas. A qualitative statement of this law can be given in several forms. Clausius states it as follows :

It is impossible for a self-acting machine unaided by any external agency, to convey heat from one body to another at a higher temperature.

Lord Kelvin gives it the slightest different form :

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

The validity of this Second Law is a matter of experience, and is not restricted to any particular substances. The reason seems to be that we are not able to deal individually with the motions of molecules, and discriminate between those with more and those with less energy, but have to deal with them in a lump. Hence it is that our treatment of the Kinetic Theory, dealing as it does with averages, presents the Second Law as a matter of course.

This is illustrated by the conception sometimes spoken of as "*Maxwell's Demon-Engine*," which is described by him as follows :¹

"But if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is at present impossible to us. For we have seen that the molecules in a vessel full of air at a uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower ones pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics."

¹ Maxwell, "*Theory of Heat*," p. 328.

CHAPTER III.

GASES WHOSE MOLECULES HAVE DIMENSIONS.

Mean Free Path.—Hitherto we have entirely disregarded the space actually occupied by the molecules themselves, and in consequence of this have paid no attention to the collisions between different molecules, except for one theorem, but have contented ourselves with the assurance that as we were considering only stable states, the countless collisions which we believe did take place still left the general distribution of the molecules, and of their speeds and their directions the same as they were before. Furthermore, it is only as the molecules have some extension that they are able to hit one another. But we wish now to enquire more minutely how far, on the average, a molecule travels after hitting one molecule before hitting the next, how often it hits other molecules, and how many collisions per second there are in any given space. The answers to these questions we must approach step by step, overcoming first one difficulty, then another.

For convenience we may at first regard all the molecules except one as fixed in their positions, and shall ask the question, how far must that molecule move before it strikes against one of the fixed molecules; or we may regard the molecule we are con-

sidering as fixed in space, and all the others, still keeping their positions relative to each other unchanged, moving in a direction just opposite to that the single molecule had, but with a speed just equal to that which it had possessed. We can then state our problem in an entirely different way: What is the probability that some portion of the surface of some particular molecule will hit the one fixed molecule within a certain time? If the original speed of the molecule was c , then in the short time dt everything in our moving system will have traveled a distance cdt , including this particular molecule, which will have described a little prism whose slant height will be cdt , and whose cross-section will be the cross-section of the molecule, which we shall call s , hence its volume will be $s c d t$. Now if this surface is to hit the fixed molecule, the molecule must lie within this little prism, hence the probability that it will hit the other molecule within the time dt is the probability that it will lie within the little volume generated by it. But if nothing further is specified as to the location of the molecule than simply that it is somewhere in a certain large volume V , which includes the little prism, the probability that it lies in the small volume is simply the ratio of the two volumes, or

$$\frac{s c d t}{V},$$

and the probability that it will hit some one of the n molecules in a unit volume is

$$n s c d t / V.$$

The probability of its hitting some portion of this surface ns is evidently proportional to the time, and hence if the time is taken long enough it is sure to hit. The mathematical expression for certainty is unity, and if we call the time in which our molecule is, on the average, just sure to hit the surface ns , τ , we have

$$\frac{nsct}{V} = 1$$

and

$$\tau = \frac{V}{nsc};$$

τ is then the average time within which the point will hit some part of the surface, and

$$\frac{1}{\tau} = \frac{nsc}{V}$$

expresses the number of such collisions per second. Since the molecule is moving with a speed c , the distance it will travel in the time τ is

$$c\tau = \frac{V}{ns} = l,$$

which is then the *mean free path* of the molecule, that is, the average distance a molecule travels between two successive collisions.

But this solution is only formal, and gives us no insight into the real occurrences. We may, however, make use of our assumption that the molecules are smooth hard spheres, then calling the diameter of

these spheres σ , whenever two spheres are in contact their centers are at a distance σ from each other. If we are considering one molecule as moving, and all the rest as fixed in their relative positions, we may regard the moving molecule as simply a point, located at the center of the actual molecule, and construct about all the other molecules spherical surfaces of radius σ with their centers at the centers of the molecules, which we may call their spheres of action. Then whenever the moving point touches one of these spherical surfaces we have the conditions for a collision, since the centers of the two molecules are separated by a distance σ . If then we consider all the fixed molecules replaced by these spheres of action, the little prisms we have imagined will be generated by these spheres, and their cross-section, which we have called s , will be the area $\pi\sigma^2$ of a central section of one of these spheres,¹ and the volume of one of the

¹ A more analytical form of demonstration is this: We are to find the probability that a portion of the surface of a moving molecule of area ds will hit the fixed molecule. In the time dt it will generate a prism of slant height cdt , and cross-section $ds \cos \theta$ where θ is the angle between the normal to the surface and the direction of motion. This makes the volume of the cylinder $ds \cos \theta cdt$. As we have no reason for assigning any particular direction to the motion of the molecule, we seek an average value of θ . We have seen (p. 34, (15)) that if all the velocity lines belonging to n molecules be drawn, if they be uniformly distributed in every direction, the number of them having directions between θ and $\theta + d\theta$ is

$$\frac{n \cdot 2\pi \sin \theta d\theta}{4\pi} = \frac{n \sin \theta d\theta}{2}.$$

We find the average value of $\cos \theta$ by multiplying by this number, inte-

prisms, or cylinders, will be $\pi\sigma^2cdt$. The volume of all the spheres of action of the molecules in a unit volume is

$$n \cdot \frac{4}{3}\pi\sigma^3.$$

Hence the remaining free volume in which our point can move is

$$V = 1 - \frac{4}{3}n\pi\sigma^3.$$

Substituting these values we have

$$l = \frac{V}{ns} = \frac{1 - \frac{4}{3}n\pi\sigma^3}{\pi n\sigma^2},$$

or if the volume of these spheres of action is so small that we can disregard it in comparison to the total volume of the gas

$$l = \frac{1}{\pi n\sigma^2},$$

and the number of collisions per second of this molecule is

$$P = \pi n\sigma^2c.$$

grating from 0 to $\pi/2$, since negative values of $\cos \theta$ do not correspond to possible collisions, and dividing by n which gives

$$\frac{1}{n} \int_0^{\pi/2} \cos \theta \frac{n \sin \theta d\theta}{2} = \frac{1}{2} \left[\frac{\sin^2 \theta}{2} \right]_0^{\pi/2} = \frac{1}{4},$$

that is, the average cross-section of the prisms is $\frac{1}{4}$ the exposed area of the molecule. This makes the volume of the average little prism $\frac{1}{4}ds cdt$. Integrating this over the sphere of action,

$$\int \frac{1}{4}ds = \frac{1}{4} \cdot 4\pi\sigma^2 = \pi\sigma^2,$$

that is, the effective area of this sphere is $\frac{1}{4}$ its total area, or the area of a central section, which we have used in our previous demonstration.

The next question which arises is, what speed is to be understood by c in this formula. We have implicitly considered that it was the average speed, \bar{c} , but only by assuming all other molecules at rest. A more accurate result would be given by considering the relative speed, r , of the moving molecule, and if its average value be \bar{r} , then the number of collisions per second of the molecule will be

$$(23) \quad P = \pi n \sigma^2 \bar{r}.$$

But the distance the molecule travels between two successive collisions is not determined by r , its relative velocity, but by c its actual velocity, hence if we have the number of collisions per second just found above, and the molecule is moving with the average speed \bar{c} , the average distance between collisions, or the mean free path is

$$l = \frac{1}{\pi n \sigma^2} \frac{\bar{c}}{\bar{r}}.$$

We must then find the value of the ratio $\frac{\bar{c}}{\bar{r}}$. This may be found approximately in the following manner:¹

¹ The approximate demonstration given in the text is due to Clausius ("Kinetische Theorie der Gase," p. 46). If we assume that the molecules have not all the same speeds, but that they have Maxwell's distribution of velocities, we may employ the following indirect demonstration given by Maxwell in his paper in *Phil. Mag.* (4), 19, 1860, reprinted in his Scientific Papers, Vol. I., paper XX., Prop. V., pp. 382-3.

Consider two sets of molecules, whose velocities we may represent by c and c' , and their relative velocity by r . Let the components be given by the three equations

$$\begin{aligned} c^2 &= u^2 + v^2 + w^2, \\ c'^2 &= (u + \xi)^2 + (v + \eta)^2 + (w + \zeta)^2, \\ r^2 &= \xi^2 + \eta^2 + \zeta^2. \end{aligned}$$

suppose the molecules to have all the same speed \bar{c} , then the relative speed of any two of them the angle between whose directions is θ will be given by the equation

$$r^2 = \bar{c}^2 + \bar{c}^2 - 2\bar{c}^2 \cos \theta = 2\bar{c}^2(1 - \cos \theta)$$

or

$$r = \bar{c}\sqrt{2(1 - \cos \theta)}.$$

Let the numbers of each kind in unit space be n and n' and the probable speeds be a and β . Then the number of the first sort having the X -components of their velocities between u and $u + du$ is, according to Maxwell's law (p. 22, (6)),

$$\frac{n}{a\sqrt{\pi}} e^{-\frac{u^2}{a^2}} du.$$

Similarly, the number of the second sort having components between $u + \xi$ and $u + \xi + d\xi$ is

$$\frac{n'}{\beta\sqrt{\pi}} e^{-\frac{(u + \xi)^2}{\beta^2}} d\xi.$$

These forms hold for any value of u , and the number of pairs of molecules, one of each sort, having the relations here given is the product

$$\frac{nn'}{a\beta\pi} e^{-\left[\frac{u^2}{a^2} + \frac{(u + \xi)^2}{\beta^2}\right]} du d\xi$$

and the total number of such pairs we may find by integrating this expression for all values of u from $-\infty$ to $+\infty$, giving

$$\frac{nn'd\xi}{a\beta\pi} \int_{-\infty}^{\infty} e^{-\left[\frac{u^2}{a^2} + \frac{(u + \xi)^2}{\beta^2}\right]} du = \frac{nn'}{a\beta\pi} J(\xi) d\xi$$

where

$$J(\xi) = e^{-\frac{\xi^2}{\beta^2}} \int_{-\infty}^{\infty} e^{-\left[u^2\left(\frac{1}{a^2} + \frac{1}{\beta^2}\right) + \frac{2u\xi}{\beta^2}\right]} du.$$

Now put

$$\frac{\sqrt{a^2 + \beta^2}}{a\beta} u = x,$$

Now the relative number of molecules whose directions make an angle between θ and $\theta + d\theta$ with any given direction has been found to be $\frac{\sin \theta d\theta}{2}$, hence we can get the average value of r , by multiplying its

$$\frac{2a\xi}{\beta\sqrt{a^2 + \beta^2}} = 2b.$$

Then

$$\begin{aligned} J(\xi) &= e^{-\frac{\xi^2}{\beta^2}} \frac{a\beta}{\sqrt{a^2 + \beta^2}} \int_{-\infty}^{\infty} e^{-(x^2 + 2bx)} dx \\ &= e^{b^2 - \frac{\xi^2}{\beta^2}} \frac{a\beta}{\sqrt{a^2 + \beta^2}} \int_{-\infty}^{\infty} e^{-(b+x)^2} d(b+x) \\ &= e^{b^2 - \frac{\xi^2}{\beta^2}} \frac{a\beta}{\sqrt{a^2 + \beta^2}} \sqrt{\pi}. \end{aligned}$$

The number above is then

$$\begin{aligned} \frac{nn'e^{b^2 - \frac{\xi^2}{\beta^2}}}{\sqrt{\pi} \sqrt{a^2 + \beta^2}} d\xi &= \frac{nn'e^{-\frac{\xi^2}{\beta^2} + \frac{\xi^2 a^2}{\beta^2(a^2 + \beta^2)}}}{\sqrt{\pi} \sqrt{a^2 + \beta^2}} d\xi \\ &= \frac{nn'}{\sqrt{\pi} \sqrt{a^2 + \beta^2}} e^{-\frac{\xi^2}{a^2 + \beta^2}} d\xi. \end{aligned}$$

Now this is the expression for the number of pairs having relative speeds, the X -component of which is between ξ and $\xi + d\xi$, the whole number of possible pairs being nn' , and is of the same form as the expression for the number of molecules having the X -components of their velocity between u and $u + du$, which is

$$\frac{n}{a\sqrt{\pi}} e^{-\frac{u^2}{a^2}} du,$$

except that the parameter is $\sqrt{a^2 + \beta^2}$ instead of a . This demonstration applies equally well to all the components of the relative speeds, and hence we conclude that the relative speeds of the two sets of mole-

value found above by this ratio, and integrating from 0 to π , since all possible directions are to be taken into account. This gives us

$$\begin{aligned}\bar{r} &= \int_0^\pi r \frac{\sin \theta d\theta}{2} = \bar{c} \int_0^\pi \sqrt{\frac{1 - \cos \theta}{2}} \sin \theta d\theta \\ &= \bar{c} \int_0^\pi \sin \frac{\theta}{2} \sin \theta d\theta = 4\bar{c} \int_0^\pi \sin^2 \frac{\theta}{2} \cos \frac{\theta}{2} d\frac{\theta}{2} \\ &= 4\bar{c} \left[\frac{\sin^3 \theta/2}{3} \right]_0^\pi = \frac{4}{3}\bar{c}.\end{aligned}$$

This gives us

cules follow Maxwell's distribution, but with the parameter $\sqrt{a^2 + \beta^2}$. Then as

$$\bar{c} = \frac{2}{\sqrt{\pi}} a,$$

$$\bar{r} = \frac{2}{\sqrt{\pi}} \sqrt{a^2 + \beta^2},$$

and if the two systems are one and the same system so that

$$a = \beta,$$

$$\bar{r} = \frac{2}{\sqrt{\pi}} \sqrt{2a^2} = \bar{c} \sqrt{2},$$

$$\frac{\bar{r}}{\bar{c}} = \sqrt{2}.$$

The same result is obtained by assuming that the one molecule, with speed \bar{c} , is moving in a space in which all the other molecules are moving with the same speed \bar{c} , but in planes perpendicular to the direction of motion of the first molecule. Then in the equation

$$r = \bar{c} \sqrt{2(1 - \cos \vartheta)},$$

$\cos \vartheta = 0$, and hence

$$\bar{r} = \bar{c} \sqrt{2}.$$

$$\frac{\bar{c}}{r} = \frac{3}{4} = .75$$

and

$$(24) \quad l = \frac{3}{4\pi n\sigma^2}.$$

The more accurate assumption that the molecules have not all the same speed, but have Maxwell's distribution gives us

$$\frac{\bar{c}}{r} = \frac{1}{\sqrt{2}} = .707,$$

a result which is only slightly different, but much more difficult to deduce. Using this value,

$$(25) \quad l = \frac{1}{\sqrt{2}\pi n\sigma^2}.$$

We do not yet know σ or n and consequently cannot use them to compute l , but l may be determined by other methods, so that this equation may later help us to find the number and size of the molecules.

We may also ask the relative number of the molecules which travel any given distance x between two successive impacts. To learn this we find the probability that a molecule will travel the distance x , before meeting another molecule. If we call this y , the probability that it will travel the distance $x + dx$ is

$$y + dy = y + \frac{dy}{dx} dx.$$

Now by the theory of probabilities, the probability that it will travel both the distance x and the distance

dx is the product of the separate probabilities. The first we have called y . The second we can find as follows: on p. 56 we found that the probability that a molecule in traveling the distance cdt should hit another molecule was

$$\frac{ns c dt}{V}.$$

Similarly the probability that in traveling the distance dx it should hit another molecule is

$$\frac{ns dx}{V} = \frac{dx}{l},$$

and the probability that it will *not* have a collision is

$$1 - \frac{dx}{l}.$$

Then the probability that it will succeed in traveling both the distance x and the distance dx without a collision is the product

$$y \left(1 - \frac{dx}{l} \right) = y + \frac{dy}{dx} dx.$$

Hence

$$\frac{dy}{dx} = -\frac{y}{l},$$

$$\frac{dy}{y} = -\frac{dx}{l},$$

$$\log y = \log C - \frac{x}{l},$$

$$y = Ce^{-\frac{x}{l}}.$$

The fact that in going no distance at all a molecule will meet with no collisions makes $y = 1$ for $x = 0$ and hence the value of the constant is $C = 1$ and

$$y = e^{-\frac{x}{l}}.$$

Corrections in the value of l will not affect the form of this function. That this is so we may find by employing this function to find the average value of the distance traveled by a molecule between two successive collisions. The probability that a molecule will travel some distance between x and $x + dx$ is given by the absolute value of $dy/dx \, dx$ which is

$$\frac{1}{l} e^{-\frac{x}{l}} dx;$$

of all the n molecules in a unit volume

$$\frac{n}{l} e^{-\frac{x}{l}} dx$$

would travel this distance, and the sum of the lengths of all their paths would be

$$\frac{nx}{l} e^{-\frac{x}{l}} dx,$$

and the average value of x would be

$$\frac{\int_0^\infty \frac{nx}{l} e^{-\frac{x}{l}} dx}{\int_0^\infty \frac{n}{l} e^{-\frac{x}{l}} dx}.$$

After dropping the common factor n , it is evident that

the integral in the denominator must have the value 1, since it is the probability that the length of path lies between 0 and ∞ . Integration gives the same result very easily. The numerator may be evaluated by integration by parts,

$$\begin{aligned}\int_0^\infty \frac{x}{l} e^{-\frac{x}{l}} dx &= \left[-x e^{-\frac{x}{l}} + \int e^{-\frac{x}{l}} dx \right]_0^\infty \\ &= \left[-l e^{-\frac{x}{l}} \right]_0^\infty = l.\end{aligned}$$

This result serves rather as a check on the correctness of the form deduced for y than as any addition to our knowledge.

Pressure. — We have now to enquire whether our previous deduction of the intensity of the pressure of a gas still holds good when the volume occupied by the molecules cannot be disregarded. In the deduction we assumed that the centers of the molecules went clear up to the walls against which the pressure was exerted, whereas they actually never came nearer than a distance $\sigma/2$ from them, then in our deduction of the pressure if we disregarded the mutual collisions of the molecules we should still have to replace the distance h between the parallel walls by $h - \sigma$, the distance a molecule would pass in going straight from one wall to the other. Now on the average each molecule travels a distance l , and that in a direction making an angle θ with the normal to the plane on which it exerts its pressure, so that the component of its motion perpendicular to the plane is $l \cos \theta$, and we can find the

effect of the impacts by taking the distance between our two planes, $h = l \cos \theta + \sigma$,

Then the sum of all the impacts of a single molecule in one second (p. 33, (14)), will be

$$\frac{m\bar{c}^2 \cos^2 \theta}{h - \sigma} = \frac{m\bar{c}^2 \cos^2 \theta}{l \cos \theta} = \frac{m\bar{c}^2}{l} \cos \theta,$$

while the number having directions between θ and $\theta + d\theta$ will be (p. 34, (15))

$$nhs \sin \theta d\theta = n(l \cos \theta + \sigma)s \sin \theta d\theta,$$

so that the total impulse due to these in one second is the product

$$\begin{aligned} & n(l \cos \theta + \sigma)s \sin \theta d\theta \frac{m\bar{c}^2}{l} \cos \theta \\ &= nm\bar{c}^2 s \frac{l \cos \theta + \sigma}{l} \cos \theta \sin \theta d\theta \end{aligned}$$

and the pressure required to equilibrate these impulses is this quantity divided by s , or the total pressure due to the molecules moving in all directions is

$$\begin{aligned} p &= \int_0^{\pi/2} \frac{nm\bar{c}^2(l \cos \theta + \sigma)}{l} \cos \theta \sin \theta d\theta \\ &= nm\bar{c}^2 \left[\int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta + \frac{\sigma}{l} \int_0^{\pi/2} \cos \theta \sin \theta d\theta \right] \\ &= nm\bar{c}^2 \left[-\frac{1}{3} \cos^3 \theta - \frac{1}{2} \frac{\sigma}{l} \cos^2 \theta \right]_0^{\pi/2} \\ &= nm\bar{c}^2 \left[\frac{1}{3} + \frac{1}{2} \frac{\sigma}{l} \right] \\ &= \frac{1}{3} nm\bar{c}^2 \left[1 + \frac{3}{2} \frac{\sigma}{l} \right] \end{aligned}$$

which may be written

$$p = \frac{1}{3} nmc^2 \left(1 + \frac{b}{v} \right)$$

or letting $nv = N$ and considering that b is small in comparison with v

$$(26) \quad p(v - b) = \frac{1}{3} Nmc^2.$$

This is evidently an extension of the equation for ideal gases and can also be written

$$(27) \quad p(v - b) = RT$$

and is of interest because it expresses almost exactly the behavior of hydrogen.

We have in obtaining this form made the substitution

$$\frac{b}{v} = \frac{3}{2} \frac{\sigma}{l}$$

which gives for

$$l = \frac{3}{4\pi n\sigma^2},$$

$$b = 2\pi v n \sigma^3 = N \cdot 2\pi \sigma^3.$$

The total volume of all the molecules is

$$N \cdot \frac{1}{6} \pi \sigma^3 = \frac{1}{12} b = .083b.$$

If we had used the value

$$l = \frac{1}{\sqrt{2\pi n\sigma^2}}$$

we should have found

$$b/v = \frac{3}{2} \frac{\sigma}{l} = \frac{3\sqrt{2\pi n\sigma^3}}{2} = \frac{3\pi n\sigma^3}{\sqrt{2}},$$

$$b = \frac{3}{\sqrt{2}} \pi N \sigma^3,$$

and the total volume of all the molecules

$$N \frac{1}{6} \pi \sigma^3 = \frac{\sqrt{2}}{18} b = .0786b.$$

Or in other words, b is 12, or 12.7 times the volume of the molecules. This correction b is much too large, for we are interested particularly in the internal pressure, rather than that upon a wall, and the value of the mean free path was deduced for motions in the interior of the gas. The collisions may be of every sort from exactly central to exactly grazing, so that the correction for an end of the path instead of being $\sigma/2$ may have any value from 0 to $\sigma/2$, on the average $\sigma/4$, and this correction will be in the direction of l , hence the pressure will be

$$\begin{aligned} p &= \int_0^{\pi/2} \frac{nmc^2(l + \frac{1}{2}\sigma)}{l} \cos^2 \theta \sin \theta d\theta \\ &= \frac{1}{3} nmc^2 \left(1 + \frac{1}{2} \frac{\sigma}{l}\right). \end{aligned}$$

giving

$$b/v = \frac{1}{2} \frac{\sigma}{l}$$

instead of $\frac{3}{2} \sigma/l$; hence b is not 12 but 4 times the volume of the molecules. This is the value found by van der Waals, while Clausius and O. E. Meyer find the ratio $4\sqrt{2}$. While the ratio is then slightly in doubt, it is still evident that b is some small multiple

of the volume of the molecules, and of the same order of magnitude.

Specific Heats. — In the case of molecules whose size cannot be entirely disregarded we can no longer assume that the only motion of the molecules is their motion of translation, or that their energy is all energy of translation. In the case of ordinary bodies of considerable dimensions we observe a continual tendency for the motion of the body to degenerate, in consequence of friction, more and more into motion of the smaller parts, and vibratory motions of greater and greater complexity and smallness, till we say their energy is dissipated in heat. In almost all terrestrial motions this tendency is quite marked, and the degradation of other forms of energy into heat is very rapid, consequently many have found difficulty in securing a satisfactory conception of the kinetic theory. It has seemed to them that with every collision of the molecules, just as with every collision between extended bodies, there must be a degradation of a large part of their energy into energy of the motion of smaller parts, so that there would be no state of real equilibrium. There is this important difference, however, between the two cases which are thus compared, even if we consider our molecules to have dimensions, the smaller parts are not indefinitely smaller than the molecules, consequently at every collision there will be a redistribution of the energy between the different possible modes of motion of the molecules, the vibratory or rotary motion of the molecule being sometimes in

such a phase at the time of the collision as to result in an increase in the energy of translation, sometimes, in such a phase as to take up more of the energy in the internal motions of the molecule; a similar phenomenon is observed when an ivory ball suspended by a thread rests in contact with the end of a metal rod. If longitudinal vibrations are excited in the rod by rubbing it, the ivory ball is thrown violently away from its position and on its return may have its motion almost checked, or it may rebound with increased violence according to the phase of the vibration of the rod.

It appears that the vibrational motions do not need to be considered in the case of *perfectly* elastic solids, such as we are considering, for the forces of deformation on collision expend themselves completely in effecting the rebound, or in other words, the coefficient of restitution of the molecules is unity. This view is upheld by Lord Kelvin, a former opponent, who says:¹

"I now see that the average tendency of collisions between elastic, vibrating solids must be to diminish the vibrational energy, provided the total energy per individual solid is less than a limit depending on the shape or shapes of the solids; and hence, as nothing is lost of the whole energy, conversion of all but an infinitesimal portion into translational and rotational energy must be the ultimate result."

In a state of equilibrium, then, there will be for any temperature and for a definite kind of molecule, a

¹ "Popular Lectures and Addresses," Vol. I., p. 464.

definite ratio between the average values of the kinetic energy of translation and of the internal motion of the molecules. Inasmuch as this distribution can only depend upon the effects of the collisions, and the phenomena of a collision can depend only on the velocities of the molecules, and not on the distances they travel between collisions, this ratio will depend only on the temperature of the gas, and not upon its density, that is, it will not be changed if the gas is expanded at constant temperature. Let us see what effect this will have upon our conceptions of the specific heats of the gas. The amount of heat required to heat the gas from the temperature T_1 to T_2 , representing the other corresponding properties by the indices 1 and 2, will consist of two parts, one, which we will call K , which increases the kinetic energy of translation of the molecules from $\frac{1}{2}Nm\bar{c}_1^2$ to $\frac{1}{2}Nm\bar{c}_2^2$, the other k , which increases the internal energy of the molecules by the amount corresponding to the rise of temperature. Then

$$K + k = \frac{1}{2}Nm(\bar{c}_2^2 - \bar{c}_1^2) + k = C_v(T_2 - T_1).$$

If the gas be heated over the same range of temperature but kept at constant pressure instead of at constant volume, besides the amount of heat just specified there would also be as in the case of an ideal gas the amount required to do the work of expansion from the volume v_1 to the volume v_2 , which we found to be

$$\frac{1}{3}Nm(\bar{c}_2^2 - \bar{c}_1^2).$$

Then the total amount of heat would be

$$\frac{5}{6}Nm(\bar{c}_2^2 - \bar{c}_1^2) + k = C_p(T_2 - T_1),$$

and the ratio of the two specific heats would be

$$\frac{C_p}{C_v} = \frac{\frac{5}{6}Nm(\overline{c_2^2} - \overline{c_1^2}) + k}{\frac{1}{2}Nm(\overline{c_2^2} - \overline{c_1^2}) + k} = \frac{\frac{5}{3}K + k}{K + k},$$

or if we call the sum $K + k = H$,

$$\frac{C_p}{C_v} = 1 + \frac{2}{3} \frac{K}{H},$$

from which we may deduce the relation

$$\frac{K}{H} = \frac{3}{2} \left(\frac{C_p}{C_v} - 1 \right).$$

In the above expression H is the energy required to raise the temperature of the gas from the temperature T_1 to T_2 , and K is the part of this energy which increases the kinetic energy of translation of the molecules. If the ratio of these two is independent of the temperature, then K/H is the ratio of the energy of translation of the molecule to the total energy. In any case

$$0 < \frac{K}{H} < 1,$$

and hence

$$1 < \frac{C_p}{C_v} < 1\frac{2}{3}.$$

The above treatment is due to Clausius. In the case of an ideal gas, which is also monatomic, K/H may approach its upper limit, unity, giving us as before the limiting value

$$\frac{C_p}{C_v} = 1\frac{2}{3}.$$

We may obtain a still more definite evaluation of the ratio of the specified heats by means of a theorem due to Boltzmann.¹ This theorem is founded upon a generalized conception associated with the phrase "degrees of freedom." The number of degrees of freedom of an object is the number of facts which must be specified in order to describe completely its state, or in the more restricted case with which we are concerned, its position. For instance, the position of a point is determined by three coördinates; these may be the three rectangular coördinates, x, y, z ; or the coördinates of the polar or geographical system, r, θ, ϕ ; or any three independent coördinates of any suitable system, but three is the smallest number of coördinates which can define the position of a point. Similarly two points are completely specified by six coördinates, but if there is some definite relation between these two points, as for instance an equation stating their distance apart, the number of coördinates necessary for a complete description is reduced by one; for instance, we may choose the three coördinates of one of the points and the two angular coördinates θ and ϕ which will give the direction of the line joining the two points, and these five coördinates will, with the knowledge of the distance of the points, determine the position of the system, which is then said to have five degrees of freedom. In general, the number of degrees of freedom is equal to the number of coördi-

¹ Boltzmann, "Gastheorie," II., pp. 125-130.

nates required to define the positions of the elements of the system, decreased by the number of independent relations existing between these elements. Hence if we call the number of atoms in the molecule of our gas n , the number of degrees of freedom cannot exceed $3n$; for a monatomic gas, with $n = 1$, it will be 3; for a diatomic gas, having the two atoms at a fixed distance from each other it will be 5, as we have just shown. For three atoms we may have, according to the arrangement, either a central atom with the two others swinging from it, or the three at the apices of a triangle. The number of degrees of freedom will then be in the first case

$$3n - 2 = 9 - 2 = 7$$

or

$$3n - 3 = 9 - 3 = 6.$$

And for more complex molecules the formulæ may be still more complex, and the number of degrees of freedom much greater. Now Boltzmann's theorem is that as a result of all the impacts between the molecules, their kinetic energy tends, on the average, to be equally distributed among the motions corresponding to the different freedoms.¹ This is best explained by applying it to the types of molecules we have just been discussing. The number of degrees of freedom associated with pure translation is evidently 3, the number of coördinates in space. Then for a mona-

¹ See Rayleigh, *Phil. Mag.* (5), 49, pp. 98-118, 1900. Kelvin, *Phil. Mag.* (6), 2, pp. 1-40, 1901.

tomic gas, having only three degrees of freedom for its molecule

$$\frac{K}{H} = \frac{3}{3} = 1$$

for a diatomic gas, whose molecule has 5 degrees of freedom,

$$\frac{K}{H} = \frac{3}{5}$$

for a triatomic gas, according to its arrangement

$$\frac{K}{H} = \frac{3}{7},$$

or

$$\frac{K}{H} = \frac{3}{6} = \frac{1}{2}.$$

We may substitute these values of K/H in the formula

$$\frac{C_p}{C_v} = 1 + \frac{2}{3} \frac{K}{H},$$

obtaining the values

$n = 1$	$\frac{C_p}{C_v} = 1.66,$
2	1.4,
3 (linked)	1.28,
3 (triangular)	1.33.

We have already mentioned the fact that the value of this ratio for mercury vapor, which is believed to be monatomic, is found to be 1.666. The diatomic

gases, oxygen, nitrogen, air (a mixture of the two preceding), hydrogen, and some others give values which average, for different experimenters, about 1.405. The haloid elements, chlorine, bromine, iodine, appear to give values in the neighborhood of 1.3, but these values are anomalous, and may be due to approaching dissociation. Of the triatomic gases, the ratio for carbon dioxide, CO_2 is given by various observers all the way from 1.265 to 1.311; for nitrous oxide, N_2O , from 1.27 to 1.311; for sulphurous oxide, SO_2 , from 1.248 to 1.262, and for hydrogen sulphide, H_2S , from 1.258 to 1.276. The agreement of these numbers with those suggested by the theoretical discussion is close enough to give the discussion great interest, and is nearly as close as the agreement between the results of different observers. There still remain, however, differences of sufficient magnitude so that they must be recognized; these we shall consider in a later chapter.

CHAPTER IV.

TRANSPORT PROBLEMS.

OUR discussion of gaseous phenomena has so far been confined to cases in which, whatever the motions of the molecules individually, the gas as a whole was at rest and in equilibrium. This state of equilibrium has been one of the fundamental assumptions upon which the treatment has rested. We have now to take up a class of problems in which we observe not equilibrium, but simply a steady state, not simply of the molecular motions, but also of the gas itself. Examples of such problems are the conduction of electricity and heat by gases; the flow of gases through tubes, and other phenomena of gaseous viscosity, and the phenomena of diffusion.

Conduction of Electricity.—Perhaps the simplest of these problems is that of the conduction of electricity under the purely hypothetical assumption that the molecules are perfect conductors of electricity. Suppose two planes, which

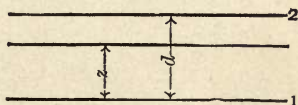


Fig. 7.

we may designate by the subscripts 1 and 2, to be at a definite distance d apart, and to be kept charged at the potentials V_1 and V_2 respectively. If we make these planes perfectly conducting plates, each mole-

cule coming in contact with one of the planes will receive from it such a charge as will bring it just to the potential of that plane. Call these charges G_1 and G_2 . If the molecules are perfect spheres of diameter σ , the electrical capacity of each molecule will be $\sigma/2$, and hence

$$G_1 = V_1 \sigma/2, \quad G_2 = V_2 \sigma/2.$$

For the sake of definiteness we may consider the potential V_2 higher than V_1 and the charge G_2 greater algebraically than G_1 . Then in any other plane intermediate between the planes 1 and 2 the potential will be intermediate between V_1 and V_2 , and the average charges of the molecules, whether by the equalizing effect of interchange of charges upon collision or by the mixture of molecules coming from the two opposite regions, will have a perfectly definite value intermediate between G_1 and G_2 . If we suppose that sufficient time has elapsed for the establishment of a steady state of conduction, and that the plates are of large area compared with the distance between them, the potential and the average charge of the molecules can be expressed as linear functions of the distance of the plane we are considering from the two planes of reference. If we take the Z -axis perpendicular to these planes, measuring z positively from the plane 1 toward the plane 2, then the potential and average molecular charges at any point are given by the expressions

$$V = V_1 + \frac{V_2 - V_1}{d} z,$$

$$G = G_1 + \frac{G_2 - G_1}{d} z,$$

which reduce to V_1 and G_1 respectively at the plane 1, where $z = 0$, and V_2 and G_2 at the plane 2, where $z = d$. The molecules arriving at any plane P , parallel to the planes 1 and 2, will each bring with them, on the average, the charges corresponding to the plane in which they experienced their last collisions. Now we have no means of knowing just what distance has been traveled by each molecule, and still less do we know what proportion of its total path between the last previous and the next following collisions has been passed before reaching this plane. But we have no reason for considering the probability that a given molecule shall strike or pass through a given portion of this plane any different from that for any other equal area; hence we must assume that the molecules passing through this plane have on the average traveled a distance equal to the mean free path of the molecule since their last previous collisions.

Then any molecule reaching a plane whose distance from the plane 1 is z , having traveled a distance l since its last collision in a direction making an angle ϑ with the normal to the plane, will have come from a plane higher, or lower than this plane by a distance $l \cos \vartheta$, that is, from a plane whose distance from the plane 1 is

$$z + l \cos \vartheta \text{ or } z - l \cos \vartheta,$$

and such molecules will bring with them on the aver-

age, the charges corresponding to these planes, that is,

$$G_1 + \frac{G_2 - G_1}{d}(z + l \cos \vartheta),$$

and

$$G_1 + \frac{G_2 - G_1}{d}(z - l \cos \vartheta),$$

If we assume that all the molecules have the same speed, \bar{c} , the molecules coming from a direction making the angle ϑ with the axis of Z will have a component velocity in the direction Z .

$$w = \bar{c} \cos \vartheta.$$

The number of such molecules in unit volume will be (p. 34, (15)),

$$\frac{n \cdot 2\pi r^2 \sin \vartheta d\vartheta}{4\pi r^2} = \frac{n}{2} \sin \vartheta d\vartheta;$$

and the number of these which will pass through unit area normal to the axis of Z in one second is

$$w \cdot \frac{n}{2} \sin \vartheta d\vartheta = \frac{1}{2} n \bar{c} \sin \vartheta \cos \vartheta d\vartheta$$

Integrating this from 0 to $\pi/2$ we get as the total number of molecules passing through unit area from one side in one second

$$\frac{1}{2} n \bar{c} \int_0^{\pi/2} \sin \vartheta \cos \vartheta d\vartheta = \frac{1}{2} n \bar{c} \left[\frac{1}{2} \sin^2 \vartheta \right]_0^{\pi/2} = \frac{1}{4} n \bar{c},$$

a result which may be found either by more complex methods, or by taking the average value of $\cos \vartheta$, $\frac{1}{2}$ (p. 59).

Each of these molecules, having come a distance l will have come from a layer whose normal distance is $l \cos \vartheta$, and the average of these values will be

$$\frac{\int_0^{\pi/2} l \cos \vartheta \cdot \frac{1}{2} n \bar{c} \sin \vartheta \cos \vartheta d\vartheta}{\int_0^{\pi/2} \frac{1}{2} n \bar{c} \sin \vartheta \cos \vartheta d\vartheta} = l \frac{\int_0^{\pi/2} \sin \vartheta \cos^2 \vartheta d\vartheta}{\int_0^{\pi/2} \sin \vartheta \cos \vartheta d\vartheta}$$

$$= l \frac{\left[-\frac{1}{3} \cos^3 \vartheta \right]_0^{\pi/2}}{\left[\frac{1}{2} \sin^2 \vartheta \right]_0^{\pi/2}} = l \frac{\frac{1}{3}}{\frac{1}{2}} = \frac{2}{3} l.$$

Using these values, the average charges brought with them by the molecules passing through the plane z are

$$G_1 + \frac{G_2 - G_1}{d} \left(z + \frac{2}{3} l \right)$$

$$G_1 + \frac{G_2 - G_1}{d} \left(z - \frac{2}{3} l \right)$$

and the total quantities carried by the molecules passing downward and upward respectively through the planes will be

$$\frac{1}{4} n \bar{c} \left[G_1 + \frac{G_2 - G_1}{d} \left(z + \frac{2}{3} l \right) \right],$$

$$\frac{1}{4} n \bar{c} \left[G_1 + \frac{G_2 - G_1}{d} \left(z - \frac{2}{3} l \right) \right].$$

The resultant current of electricity passing through unit area of the plane will be given by the difference of these quantities, which is,

$$\frac{1}{4} n \bar{c} \frac{G_2 - G_1}{d} \frac{4}{3} l = \frac{1}{3} n \bar{c} l \frac{G_2 - G_1}{d},$$

or, if the molecules are perfect spheres,

$$\frac{1}{3} n \bar{c} l \frac{V_2 - V_1}{d} \frac{\sigma}{2} = \frac{1}{6} n \bar{c} l \sigma \frac{V_2 - V_1}{d},$$

in which $(V_2 - V_1)/d$, which may also be written $\partial V / \partial Z$, is the potential gradient, and $\frac{1}{6} n \bar{c} l \sigma$ the specific conductivity. If we give to l its value (p. 64, (24)) $3/4\pi n \sigma^2$, computed on the assumption that all the molecules have the same speed, we have for the conductivity,

$$\frac{1}{6} n \bar{c} \sigma \frac{3}{4\pi n \sigma^2} = \frac{1}{8} \frac{\bar{c}}{\pi \sigma},$$

an expression involving only \bar{c} and σ .

This deduction can make no claim to numerical accuracy, on account of the arbitrary assumptions and approximations made. Irregularities in the shape of the molecules might change the electrical capacity slightly but would not seriously affect the numerical results. Of more importance would be the influence of the mutual forces exerted between the charged molecules upon their motions, which we have neglected entirely. Further we have made our deductions only approximate by assuming that all the molecules have the same speed, and by averaging separately the effects of the inclination of the paths of the molecules upon the charges carried by the molecules, and upon the numbers of molecules passing through the plane. Boltzmann¹ using more exact methods finds the conductivity to be

$$\frac{k}{2} \bar{c} n \sigma,$$

¹ "Gastheorie," I., p. 80.

where k is a definite integral whose value he finds to be .35027, thus making the numerical coefficient .17514, while the approximate method we have employed makes it $\frac{1}{6} = .1667$

These values which we have obtained are based upon the fundamental assumption that the molecules are perfect conductors, an assumption which is confessedly not in accordance with the facts as we know them, and hence the formulæ deduced cannot be employed to compute, from observation upon the conductivity, numerical values of σ , the diameter of the molecules.

Viscosity of Gases.—This problem differs from the one just treated in that the difference between the molecules in different regions is a difference in velocities, and not a simple difference in some extraneous quality, which does not affect the motions of the molecules. We shall suppose that the gas we are considering is moving as a whole in one direction, but different portions with different speeds. For convenience we may take the direction of the motion as the direction of the X -axis; for the sake of definiteness and simplicity we shall assume that all the gas in any plane perpendicular to the Z -axis has the same general motion, and since all motion is relative, we will take the plane 1 (Fig. 7) as the plane of no motion. Call the velocity of the plane 2 in its own plane in the direction of X , V_0 . Then if the distance of any point perpendicularly from the plane 1 toward the plane 2 be called z , and if the motions of the gas are steady,

we may expect that the general motion of the gas at any intermediate point will be a linear function of its distance from the plane 1, or

$$V = Z \frac{\partial V}{\partial Z},$$

where, if d be the distance between the planes 1 and 2,

$$\frac{\partial V}{\partial Z} = \frac{V_0}{d}.$$

This gives us an expression for the motion of the gas as a whole. The motions of the individual molecules will be the resultant or sum of the motions they would have if the gas were at rest, and the motion of that part of the gas in which they happen to be, so that the three components of their velocities will be not u, v, w , but $u + V, v, w$, where u, v, w , and their resultant c represent the ordinary velocity of a molecule when the gas as a whole is at rest. Now the velocity V , even if it corresponded to a very violent motion of the gas, would still be very small as compared with c , the average speed of the individual molecules. A wind of fifty miles an hour is a destructive gale, and one of a hundred miles an hour is capable of destroying everything that comes in its path, while c , for air, is of the order of a thousand miles an hour. Consequently we can without serious error regard the molecules in one layer as differing from the molecules in another layer only in the possession of different quantities of directed momenta, the direction of these being the same for all layers, namely the direction of the

motion of the gas, parallel to the X -axis, but the amount varying from layer to layer with the value of z .

From the dynamical standpoint the effect of these differences of speed upon the two planes is a force dragging or holding back the plane 2 and a force tending to pull along the plane 1. Experiment and theory both indicate that this force, which seems to be due to an internal friction of the gas is equal in amount for the two planes, is proportional to their area, to their difference of speed, and inversely proportional to the distance between the planes. Then the force acting on a unit area of either plane may be written

$$F = \eta \frac{V_0}{d},$$

where η , the factor of proportionality, may depend upon the nature of the gas, and is called its *Coefficient of Viscosity*.

From the molecular standpoint molecules striking the plane 2, will have on leaving it, by reason of their friction with it, or momentary entanglement with it, on the whole an excess of velocity V_0 in the direction of the motion of the plane and receive from it whatever addition of momentum is necessary to bring them up to this velocity. Similarly molecules striking the plane 1 will give up to it all their excess of momentum, and leave it with velocities such as they would have if the gas as a whole were at rest. This transfer of momentum from the plane 2 to the molecules of the gas, and from these to the plane 1 constitutes the

mechanism of the forces observed. The force must be numerically equal to the amount of momentum transferred in one second.

This transfer will take place uniformly, on the whole, throughout the body of the gas, hence we have only to find the excess of this directed momentum carried in one direction by the molecules of the gas through any plane parallel to the planes 1 and 2 over that carried in the other direction. The method of treatment is entirely analogous to that of the last problem. The molecules coming from above will come from an average height $\frac{2}{3} l$ above the plane we are considering, and will carry with them downward through the plane an average directed momentum

$$m \frac{V_0}{d} (z + 2l/3),$$

while those from below will bring an average of

$$m \frac{V_0}{d} (z - 2l/3).$$

The number of molecules passing through unit area of the plane in one second will be, as before,

$$\frac{1}{4} n \bar{c},$$

so that the total amount of directed momentum carried by the molecules passing downward and upward respectively through unit area in one second is

$$\frac{1}{4} n m \bar{c} \frac{V_0}{d} (z + \frac{2}{3} l),$$

$$\frac{1}{4} n m \bar{c} \frac{V_0}{d} (z - \frac{2}{3} l),$$

and the excess, which is equivalent to the force exerted on the plane, is

$$\frac{1}{4}nm\bar{c}\frac{V_0}{d} \cdot \frac{4}{3}l = F = \eta \frac{V_0}{d}$$

whence

$$(28) \quad \eta = \frac{1}{3}nm\bar{l}\bar{c},$$

an expression whose form reminds us of that for the pressure,

$$(1) \quad p = \frac{1}{3}nm\bar{c}^2,$$

a length l replacing in it a velocity c . It will be noted however that the dimensions are entirely different. The more exact value found by Boltzmann¹ is

$$knm\bar{l}\bar{c},$$

where k has the value .350271, not very different from the coefficient we have found, $\frac{1}{3}$. As the viscosity of a gas can be determined experimentally, it is evident that the formula

$$\eta = \frac{1}{3}nm\bar{l}\bar{c},$$

or the more exact form given by Boltzmann may be employed to compute the value of l . Some of the data and the results thus obtained will be given in a later chapter.

Substituting in the formula for l its value (p. 64, (24)),

$$l = \frac{3}{4\pi n\sigma^2},$$

$$\eta = \frac{1}{3}nm\bar{c} \cdot \frac{3}{4\pi n\sigma^2} = \frac{m\bar{c}}{4\pi\sigma^2}.$$

¹ "Gasttheorie," I., p. 81.

This value would by more accurate methods of deduction only have its numerical constants slightly changed, its general form would remain the same. It is evident that this formula cannot be employed to determine the value of either m or σ unless we already know the value of one of them.

The last formula shows that the coefficient of viscosity may depend upon the mass of the molecules, upon their size, since σ^2 is involved, and upon the temperature, being proportional to the square root of the latter; it will be independent of the pressure or density of the gas, though not of its kind since n does not appear. We may express the viscosity directly as a function of the temperature by eliminating the velocity by the equations

$$(28) \quad \begin{aligned} pv &= \frac{1}{3} N m \bar{c}^2 = RT, \\ \eta &= \frac{1}{3} n m l \bar{c}, \end{aligned}$$

$$(\bar{c})^2 : \bar{c}^2 = \frac{4}{\pi} : \frac{3}{2}.$$

These give us

$$\bar{c}^2 = \frac{3RT}{Nm},$$

$$\bar{c} = \sqrt{\frac{8\bar{c}^2}{3\pi}} = 2 \sqrt{\frac{2RT}{\pi Nm}},$$

$$\eta = \frac{2}{3} n m l \sqrt{\frac{2RT}{\pi Nm}},$$

which becomes if, we use the other value of l ,

$$\begin{aligned}
 (25) \quad l &= \frac{1}{\sqrt{2\pi n\sigma^2}}, \\
 \eta &= \frac{2}{3} \frac{nm}{\sqrt{2\pi n\sigma^2}} \sqrt{\frac{2RT}{\pi Nm}} \\
 &= \frac{2m}{3\sigma^2} \sqrt{\frac{RT}{\pi^3 Nm}} \\
 &= \frac{2}{3\sigma^2} \sqrt{\frac{mRT}{\pi^3 N}}.
 \end{aligned}$$

In which Nm is the quantity of gas taken as the standard amount in computing the value of R , for instance one gram molecule, so that R/Nm is a constant whose value depends upon the particular gas under consideration, while R/N in the last expression is independent of the kind of gas. This form shows even more strikingly than the other the fact that the viscosity of the gas depends only upon the kind of the gas and its temperature.

Experiments upon the viscosity of gases have shown that the viscosity increases with the temperature, but is not exactly proportional to the square root of the absolute temperature. Attempts have been made, but with only partial success, to devise formulæ which shall be able to express the dependence of the viscosity upon the temperature. Two causes for variation from this simple formula are suggested, the mutual attractions of the molecules, and change of aggregation, particularly dissociation, causes whose general effects are to be discussed in later chapters.

We have seen that according to the formula developed the viscosity of a gas should be independent of the pressure or density. Experiments by many able investigators have shown that this is true for a wide range of pressures, but below $1/60$ of an atmosphere,¹ and for some gases above 30 atmospheres² there is some variation with the pressure. It is indeed to be expected that this formula would fail for extreme cases, since it was developed under the assumptions that the straight portions of the paths of the molecules were very long as compared with the curved portions associated with their mutual impacts, which is less nearly justified at extremely high pressure, and that the distances between the solid surfaces on which the drag is exerted are large as compared with the mean free path, an assumption whose validity fails when the pressure becomes exceedingly small. The discussion of this last case will be taken up in connection with the next topic.

Conduction of Heat. — The statement of this problem is entirely similar to that of the two preceding problems. The gas at the plane 1 is at the temperature T_1 , that is, it has a mean value of the square of the velocities of the molecules $\overline{c_1^2}$, and the corresponding values at the plane 2 are T_2 and $\overline{c_2^2}$. The temperature gradient will be

$$\frac{T_2 - T_1}{d}$$

¹ Kundt & Warburg, *Pogg. Ann.*, 1875, CLV., pp. 337, 525.

² Warburg & Babo, *Wied. Ann.*, 1882, XVII., p. 390.

and the corresponding rate of change in the mean square of the velocities will be

$$\frac{\overline{c_2^2} - \overline{c_1^2}}{d},$$

so that the mean square of the velocities of the molecules in any plane whose distance from the plane 1 measured toward the plane 2 is z will be

$$\overline{c_1^2} + z \frac{\overline{c_2^2} - \overline{c_1^2}}{d}.$$

We shall assume that the differences of temperatures and density are small, and that the number of molecules passing through unit area in each direction in unit time, which must be the same, is represented by the expression previously deduced, namely

$$\frac{1}{4}n\bar{c},$$

and that the molecules come from the same average vertical distance $\frac{2}{3}l$ above or below this plane, then remembering that the energy of a molecule is given by the expression $\frac{1}{2}mc^2$, the molecules passing downward through unit area of the plane in one second will carry with them the energy

$$\begin{aligned} \frac{1}{4}n\bar{c} \cdot \frac{1}{2}m \left[\overline{c_1^2} + \frac{\overline{c_2^2} - \overline{c_1^2}}{d} \left(z + \frac{2}{3}l \right) \right] \\ = \frac{1}{8}nm\bar{c} \left[\overline{c_1^2} + \frac{\overline{c_2^2} - \overline{c_1^2}}{d} \left(z + \frac{2}{3}l \right) \right], \end{aligned}$$

and similarly the amount carried by those passing upward will be

$$\frac{1}{8}nm\bar{c}\left[\bar{c}_1^2 + \frac{\bar{c}_2^2 - \bar{c}_1^2}{d}\left(z - \frac{2}{3}l\right)\right],$$

while the excess of the amount of energy carried downward over that carried upward will be

$$\frac{1}{8}nm\bar{c} \cdot \frac{\bar{c}_2^2 - \bar{c}_1^2}{d} \cdot \frac{4}{3}l = \frac{1}{6}nm\bar{c} \frac{\bar{c}_2^2 - \bar{c}_1^2}{d}.$$

Since the heat energy of the standard amount of gas, which we have represented by $\frac{1}{2}Nm\bar{c}^2$, may be even more accurately represented by $C_v T$, we may substitute the latter expression for the former, giving us

$$\frac{1}{3}\frac{n}{N}C_v\bar{lc}\frac{T_2 - T_1}{d},$$

in which

$$\frac{1}{3}\frac{n}{N}C_v\bar{lc}$$

is the coefficient of thermal conductivity. The ratio n/N is defined by the equation $N = nv$ as the reciprocal of v , the volume occupied by the standard amount of our gas, hence the coefficient reduces to the form

$$\frac{1}{3}\frac{C_v}{v}\bar{lc},$$

where C_v/v is the thermal capacity of a unit volume of the gas.

Putting for l its value we have

$$\frac{1}{3}\frac{C_v\bar{c}}{v}\frac{3}{4\pi n\sigma^2} = \frac{C_v\bar{c}}{4\pi N\sigma^2},$$

which, however, cannot be used to compute either N or σ unless one of them is previously known.

Like the viscosity the thermal conductivity is proportional to the square root of the absolute temperature, and independent of the pressure or density. Using the same substitution as before the coefficient becomes

$$\frac{C_v}{2N\sigma^2} \sqrt{\frac{RT}{\pi^3 Nm}} = \frac{1}{2(\gamma - 1)\sigma^2} \sqrt{\frac{R^3 T}{\pi^3 N^3 m}},$$

where γ is the ratio of the two specific heats.

The applicability of this formula to actual gases is subject to limitations similar to those mentioned in connection with the viscosity of gases. It appears that the departure of the heat conductivity of rarefied gases from constancy is intimately associated with the breaking down of the condition that the distance between the solid surfaces between which the heat is conducted is large in comparison with the mean free path of the molecules. There must be a slight discontinuity in temperature at these surfaces, since the molecules just in contact with each surface, instead of being at the temperature of the surfaces, can be regarded as made up of two classes; one, of those molecules which are approaching the surface, and hence, coming from cooler portions of the gas, are at a lower temperature than the solid surface, and the other consisting of molecules just leaving the surface, and at its temperature; the layer of gas next to the surface will then consist of a mixture of the mole-

cules of these two classes, and will have an average temperature slightly lower than that of the solid surface it touches, or at the other surface slightly higher. It is possible to take account of this variation by introducing as a correction to the distance d , for each surface, an amount equal to the distance from the geometrical position of the surface back to the plane where the gas would have the same temperature as the surface on the supposition that the temperature exhibited in that region the same linear variation with the distance which it does exhibit between the planes. This correction distance seems to be proportional to the mean free path, and the ratio has been determined for air and hydrogen by E. Gehrcke¹ who finds that for the former the correction at one surface is 1.83 times the mean free path, while for hydrogen it is 5.78 times that distance.

Diffusion.—This problem differs from those just discussed in two respects; the quantity which is carried from one region to the other is composed of the molecules of the gas itself, and as diffusion is ordinarily of one gas into another, there are two kinds of molecules present. We shall as before take our Z -axis in the direction in which the diffusion takes place, but we shall change our notation so that the subscript 1 will apply to molecules of the first kind, and the subscript 2 to molecules of the second kind. Then at any point the number of molecules of the first kind per unit volume will be n_1 , the mass of each molecule m_1 , and

¹ *Drude's Ann.*, 2, p. 112, 1900.

its velocity c_1 ; while the corresponding quantities for the second kind will be n_2 , m_2 and c_2 . Let the position of the plane perpendicular to the direction of the diffusion be given by its coördinate, z , and for the sake of definiteness the positive direction be so chosen that for larger values of z the density of the first kind of gas shall be greater, that is, $\partial n_1 / \partial z > 0$; then the opposite will usually be true for the second gas, namely $\partial n_2 / \partial z < 0$. The molecules of the first kind passing downward through the plane z may be assumed as before to have come an average distance l_1 , but in various directions, so that they may be spoken of as coming from a plane whose coördinate is $z + l_1 \cos \vartheta$. We have previously found the average value of this expression to be $z + \frac{2}{3}l_1$. If n_1 be the number of molecules per unit volume at the plane z , the corresponding number at the plane $z + \frac{2}{3}l_1$ will be

$$n_1 + \frac{2}{3}l_1 \frac{\partial n_1}{\partial z},$$

and the number from this plane passing downward through unit area of the plane z in unit time will be, supposing them all to have the same speed \bar{c}_1 ,

$$\frac{1}{4} \left(n_1 + \frac{2}{3}l_1 \frac{\partial n_1}{\partial z} \right) \bar{c}_1.$$

Similarly the number of molecules of the first kind passing upward through the plane z in unit time will be

$$\frac{1}{4} \left(n_1 - \frac{2}{3}l_1 \frac{\partial n_1}{\partial z} \right) \bar{c}_1,$$

and the excess of the number of those passing downward over those passing upward, which is the measure of the rate of diffusion will be the difference of these two quantities, or

$$\frac{1}{3}l_1c_1\frac{\partial n_1}{\partial z}.$$

Simply interchanging subscripts and signs we have the excess of diffusion of the molecules of the second kind *upward*

$$-\frac{1}{3}l_2c_2\frac{\partial n_2}{\partial z},$$

which is intrinsically positive when

$$\frac{\partial n_2}{\partial z} < 0.$$

In seeking to find the relation between the theoretical discussion and actual cases of diffusion we have to distinguish between different types of problems according as (a) the two kinds of molecules are alike or different as regards mass, size or any characteristics which might affect their motion, (b) the total pressure exerted by the two gases is the same or not in all parts of the region in which the diffusion takes place.

The simplest case is that in which the two kinds of molecules differ in no respect except that we may suppose them capable of being identified as to their kind, as for instance by a difference of color. Then we will have $m_1 = m_2$, $c_1 = c_2$, $l_1 = l_2$, and for these quantities may drop the subscripts. The pressure and temperature being supposed uniform throughout the space, the

sum of the number of molecules of the two kinds per unit volume will be a constant,

$$n_1 + n_2 = n$$

and the rate of diffusion of the molecules of each kind will be

$$\frac{1}{3}\bar{l}c \frac{\partial n_1}{\partial z}$$

the rates being the same, but the directions opposite for the two kinds, while the gas as a whole will remain stationary. The mass of each kind of gas passing through unit area in one second will be this expression multiplied by m , the mass of the molecule, that is,

$$m \cdot \frac{1}{3}\bar{l}c \frac{\partial n_1}{\partial z} = \frac{1}{3}\bar{l}c \frac{\partial n_1 m}{\partial z}$$

where the derivative $\partial n_1 m / \partial z$ expresses the rate of change of the density of the first kind of gas along z . The transformations effected by substituting for l its approximate value and introducing the temperature in place of c are entirely similar to those observed in the previous cases, and need no further discussion.

If we assume that only one kind of gas is present, and that the pressure is not uniform, we have $n_2 = 0$, and our problem becomes one of dynamics, the question of the speed of a wind due to a given difference of pressure or density; if the diffusion is to take place through tubes or orifices of finite dimensions, the friction of the gas against the wall of the tubes will cause the predominant phenomena to be those of viscosity.

If on the other hand we attempt to solve the prob-

lem of the inter-diffusion of two gases we are confronted by two difficulties: the value of l_1 , the mean free path of a molecule of the first kind, is certainly not the same as if only the n_1 molecules of the first kind were present, for there is also the probability of collisions with molecules of the second kind, and it is probably not the same that it would be if all the $n_1 + n_2$ molecules were of the same kind, and the numbers of the two kinds of molecules passing through any plane in the opposite directions are not necessarily the same, and hence there must result an inequality of pressure in different regions, or else a general drift of the mixture of gases just sufficient to make up for the difference in their diffusions, the former being observed in the case of the diffusion of gases through a porous wall, as of plaster of Paris, while the latter must occur in free diffusion.

The mean free path for a molecule of either kind in a mixed gas made up of two components may be found approximately as follows:

We have found (p. 60) that the average number of collisions per second of a single molecule is

$$(23) \quad P = \pi n \sigma^2 \bar{r}.$$

If we designate the quantities referring to the impacts of a molecule of the first kind against molecules of the second by the subscript 12, this formula takes the form

$$P_{11} = \pi n_1 \sigma_1 \bar{r}_{11}$$

$$P_{12} = \pi n_2 \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \bar{r}_{12},$$

where P_{11} is the number of collisions with molecules of the first kind, and P_{12} with those of the second kind. $(\sigma_1 + \sigma_2)/2$ will be the distance between the centers of the two molecules of different kinds at the instant of collision. The total number of collisions per second will be

$$P_1 = P_{11} + P_{12}.$$

$\overline{r_{11}}$ is identified with \overline{r} as previously found. $\overline{r_{12}}$, however, the relative speed of two molecules of different kinds, is still to be found. If we make the assumption that all the molecules of the first kind have the same speed, $\overline{c_1}$, and all those of the second the same speed $\overline{c_2}$, the relative speed of two molecules of different kinds will be given by the equation

$$r_{12}^2 = \overline{c_1}^2 + \overline{c_2}^2 - 2\overline{c_1}\overline{c_2} \cos \vartheta.$$

If we take for $\cos \vartheta$ the average value 0,¹ as if the molecule of the first kind were projected with the velocity $\overline{c_1}$ into a region occupied by molecules of the other kind all moving with the speed $\overline{c_2}$ in planes perpendicular to the direction of the newcomer, we have

$$\overline{r_{12}}^2 = (\overline{c_1})^2 + (\overline{c_2})^2.$$

From the equilibrium of temperature which may be assumed we have

$$m_1(\overline{c_1})^2 = m_2(\overline{c_2})^2,$$

¹See note, pp. 60-63, in which the formula $\overline{r} = 2/\pi \sqrt{a^2 + \beta^2}$ would reduce to

$$\overline{r_{12}} = \sqrt{(\overline{c_1})^2 + (\overline{c_2})^2}.$$

$$(\bar{c}_2)^2 = \frac{m_1}{m_2} (\bar{c}_1)^2,$$

$$\bar{r}_{12}^2 = (\bar{c}_1)^2 \left(1 + \frac{m_1}{m_2} \right),$$

$$\bar{r}_{12} = \bar{c}_1 \sqrt{1 + \frac{m_1}{m_2}},$$

which, if the two kinds of molecules have the same mass, reduces to

$$\bar{r} = \bar{c} \sqrt{2},$$

one of the forms previously obtained. Inspection shows that the values of \bar{r}_{12} and \bar{r}_{21} , which can be obtained by interchanging the subscripts are the same, and that when the two kinds of molecules have very different speeds and masses the relative speed, is very nearly the average speed of the lighter and swifter molecule; as, for instance, if 1 refer to hydrogen and 2 to oxygen,

$$\frac{m_1}{m_2} = \frac{1}{16},$$

$$\bar{r}_{12} = \bar{c}_1 \sqrt{1 + \frac{1}{16}} = \bar{c}_1 \frac{1}{4} \sqrt{17} = 1.0308 \bar{c}_1,$$

$$\bar{r}_{21} = \bar{c}_2 \sqrt{1 + 16} = \bar{c}_2 \sqrt{17} = 4.1231 \bar{c}_2,$$

which are equal, as has just been stated, since

$$c_1 : c_2 = 4 : 1.$$

The total number of collisions per second of a molecule of the first kind then becomes

$$\begin{aligned}
 P_1 &= P_{11} + P_{12} = \pi n_1 \sigma_1^2 \bar{r}_{11} + \pi n_2 \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \bar{r}_{12}, \\
 &= \sqrt{2} \pi n_1 \sigma_1^2 \bar{c}_1 + \sqrt{1 + \frac{m_1}{m_2}} \pi n_2 \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \bar{c}_1,
 \end{aligned}$$

and the mean free path of such molecules

$$l_1 = \frac{\bar{c}_1}{\bar{P}_1} = \frac{1}{\sqrt{2} \pi n_1 \sigma_1^2 + \sqrt{1 + \frac{m_1}{m_2}} \pi n_2 \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2},$$

and their rate of diffusion will be

$$\begin{aligned}
 \frac{1}{3} l_1 \bar{c}_1 \frac{\partial n_1}{\partial z} \\
 &= \frac{\bar{c}_1}{3 \sqrt{2} \pi n_1 \sigma_1^2 + 3 \sqrt{1 + \frac{m_1}{m_2}} \pi n_2 \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2} \frac{\partial n_1}{\partial z},
 \end{aligned}$$

an expression which depends upon the sizes, numbers and relative masses of the two kinds of molecules as well as upon their temperature and pressure. Similarly the rate for molecules of the other kind will be

$$\begin{aligned}
 \frac{1}{3} l_2 \bar{c}_2 \frac{\partial n_2}{\partial z} \\
 &= \frac{\bar{c}_2}{3 \sqrt{2} \pi n_2 \sigma_2^2 + 3 \sqrt{1 + \frac{m_2}{m_1}} \pi n_1 \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2} \frac{\partial n_2}{\partial z}
 \end{aligned}$$

These two values will probably differ somewhat, so that diffusion at these rates would result in an excess of pressure in one part of the system over that in

other parts, with a consequent general drift of the mixture, which is measured by the difference of these two coefficients, of which the two kinds are present in the proportions of n_1 and n_2 , so that the total drift will be

$$\frac{\overline{c_1}}{3\sqrt{2}\pi n_1\sigma_1^2 + 3\sqrt{1 + \frac{m_1}{m_2}\pi n_2\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2}} - \frac{\overline{c_2}}{3\sqrt{2}\pi n_2\sigma_2^2 + 3\sqrt{1 + \frac{m_2}{m_1}\pi n_1\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2}}$$

and the corrected coefficient for the first kind of molecules will be the original coefficient diminished by n_1/n times this drift, where $n = n_1 + n_2$, which reduces to

$$\begin{aligned} & \frac{n_2}{n} \frac{\overline{c_1}}{3\sqrt{2}\pi n_1\sigma_1^2 + 3\sqrt{1 + \frac{m_1}{m_2}\pi n_2\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2}} \\ & + \frac{n_1}{n} \frac{\overline{c_2}}{3\sqrt{2}\pi n_2\sigma_2^2 + 3\sqrt{1 + \frac{m_2}{m_1}\pi n_1\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2}} \\ & = \frac{1}{3\pi n} \left\{ \frac{\overline{c_1}}{\sqrt{2} \frac{n_1}{n_2}\sigma_1^2 + \sqrt{1 + \frac{m_1}{m_2}\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2}} \right. \\ & \quad \left. + \frac{\overline{c_2}}{\sqrt{2} \frac{n_2}{n_1}\sigma_2^2 + \sqrt{1 + \frac{m_2}{m_1}\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2}} \right\}. \end{aligned}$$

This formula may be simplified so as to be compared with experimental results in either of the two ways. Some have assumed that the rate of diffusion depends only upon the mutual collisions of molecules of different kinds, but not upon those of molecules of the same kinds. Upon this assumption the expression above reduces to

$$\begin{aligned} \frac{1}{3\pi n} \left\{ \frac{\bar{c}_1}{\sqrt{1 + \frac{m_1}{m_2} \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2}} + \frac{\bar{c}_2}{\sqrt{1 + \frac{m_2}{m_1} \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2}} \right\} \frac{\partial n_1}{\partial z} \\ = \frac{\sqrt{\bar{m}_2 \bar{c}_1} + \sqrt{\bar{m}_1 \bar{c}_2}}{3\pi n \sqrt{m_1 + m_2} \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2} \frac{\partial n_1}{\partial z}, \end{aligned}$$

which may be reduced, since $\bar{c}_2 = \bar{c}_1 \sqrt{\frac{m_1}{m_2}}$, to the form

$$\frac{\sqrt{1 + \frac{m_1}{m_2} \bar{c}_1}}{3\pi n \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2} \frac{\partial n_1}{\partial z}.$$

n may be eliminated and the pressure, p , be introduced, by the equation

$$p = \frac{1}{3} n m_1 \bar{c}_1^2 = \frac{\pi}{8} n m_1 (\bar{c}_1)^2,$$

which gives

$$\frac{m_1 \sqrt{1 + \frac{m_1}{m_2} (\bar{c}_1)^2} \frac{\partial n_1}{\partial z}}{24p \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2}.$$

According to this formula the coefficient of diffusion in terms of the change of density of the molecules of the first kind is independent of the relative proportions of the two kinds of molecules present, but varies inversely as the pressure, and directly as the $\frac{3}{2}$ power of the temperature. Expressed in terms of the pressure gradient, which is itself proportional to the temperature, the rate of diffusion is

$$\frac{\sqrt{1 + \frac{m_1}{m_2} \bar{c}_1^2} \frac{\partial p_1}{\partial z}}{3\pi p \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2},$$

in which the coefficient is proportional only to the square root of the temperature.

The assumption that the rate of diffusion depends only upon the collisions between unlike molecules seems improbable, and justifiable only as a first approximation. The final decision between the special formula just given and the more general one must be made on the basis of experiment, but the discrepancies in experiments so far made are such as to render any decision based upon them doubtful. For the majority of such experiments a sufficiently accurate approximation to the general formula may be made by putting $n_1 = n_2$, which gives

$$\frac{1}{3\pi n} \left\{ \frac{\bar{c}_1}{\sqrt{2}\sigma_1^2 + \sqrt{1 + \frac{m_1}{m_2} \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2}} + \frac{\bar{c}_2}{\sqrt{2}\sigma_2^2 + \sqrt{1 + \frac{m_2}{m_1} \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2}} \right\}.$$

A sharp discrimination might be made by testing the diffusion when only a very slight amount of one of the gases present, when the diffusion will approach the limiting value for $n_2 = 0$, which is

$$\frac{\bar{c}_2}{3\pi n \sqrt{1 + \frac{m_2}{m_1} \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2}}.$$

For a more exhaustive discussion the reader is referred to the work of O. E. Meyer.¹ The notation there employed is quite different, and the constant obtained is slightly different, 8 appearing in the place of 3π in the last formula given.

¹ "The Kinetic Theory of Gases," pp. 247-276.

CHAPTER V.

CHANGE OF STATE.

ON account of the greater simplicity of the phenomena of the gaseous state, the formulæ connecting these phenomena and the kinetic theory for this state were developed much earlier and more rapidly and completely than the corresponding formulæ and theory for the liquid and solid states.

Clausius early pointed out some of the general considerations which must lie at the basis of a kinetic theory of liquids, and in particular gave us a sort of picture of the processes which must take place in the vaporization of a liquid or in the condensation of a vapor; the way in which these processes take place we have attempted to describe very briefly at the end of the introduction. Since we have a fairly definite kinetic theory of gases, this transition between the liquid and gaseous state has seemed to furnish a particularly available method of finding out what is the behavior of the molecules of a liquid. In order that we may do this with the greater confidence, we shall here review some of the familiar facts regarding change of state and deduce briefly from thermodynamical considerations some equations which we may find interesting or useful.

In the case of an ordinary liquid, such as water, if

heat be applied to it, there results a slight expansion, and increase of temperature, and perhaps some slight vaporization from the surface, which however may be prevented by having the liquid confined so that there is no free space above it; if the pressure is kept constant and heat still added a temperature is reached at which vapor tends to form not simply at the surface of the liquid but also in bubbles within the body of the liquid; if still more heat is added, and the pressure still kept constant, vaporization continues, with great increase of volume but no accompanying rise of temperature until the whole liquid is vaporized; after that, further addition of heat results in rise of temperature and increase of volume as in any gas. A more complete and systematic study can be made by plotting the volume of the substance as the abscissa, and its pressure as ordinate, and drawing the isothermal curves for different temperatures. A good example is the classical work of Andrews on carbon dioxide, the diagram for which is found in most text-books on heat. He found that the isothermals for this substance were of two kinds, those for higher temperatures being curved throughout their whole length and of varying steepness, but never horizontal, while below a certain temperature they seemed to consist of three parts characteristically different, a very steep part which related to the substance in its liquid state, another curved part which related to the vapor state, and between them a straight horizontal portion, which referred to the substance when partly in the liquid and

partly in the vapor state. We may draw through the ends of these straight portions where they join the part of the curve corresponding to the liquid state a curve which we shall call the "water line," and similarly through the other ends of these straight portions a curve which we shall call the "steam line."

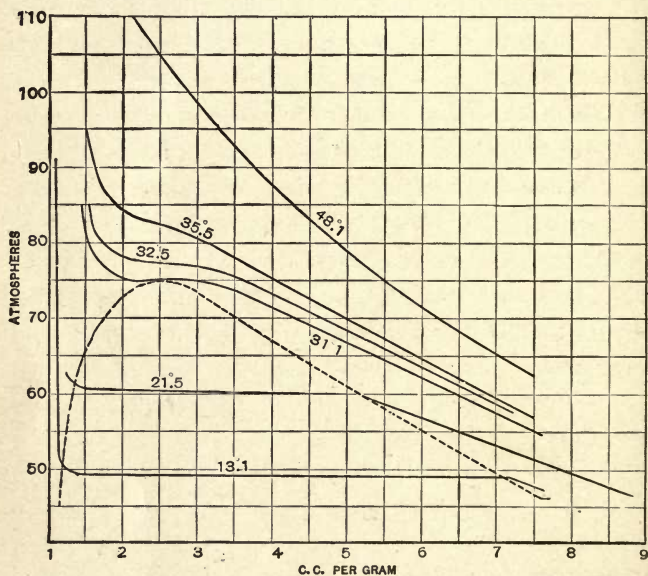


Fig. 8.

Andrews' experiments and many others show that the water line and steam line join at a point which is commonly known as the CRITICAL POINT. The isothermals above this point have no horizontal part, those below have the portion between the water and steam lines horizontal, while the isothermal through the

critical point has at that point a point of inflection where it is horizontal also, but it is not so at any other point of its whole length. All these properties may be shown by means of a surface, which has for its three coördinates the pressure, volume and temperature of the substance. The accompanying figure is

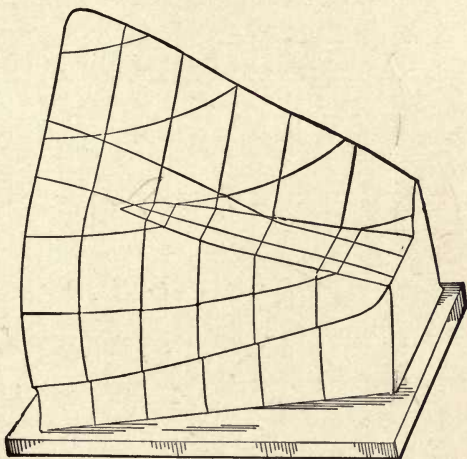


Fig. 9.

reproduced from a photograph of a model of such a surface, which belongs to the University of California; in it the temperature is measured vertically upward, so that a horizontal section gives an isothermal curve. As the figure is placed pressure is measured positively to the left, and volume forward, away from the observer. The portion of the surface which appears nearly plane represents the area of the diagram between the water

and steam lines, corresponding to the coexistence of the liquid and vapor phases of the substance. A more accurate representation of the facts would have made this part of the surface strongly convex upward, as a vertical section parallel to the axis of pressures gives the curve of the tension of the saturated vapor, in which the tension is found by experiment to increase more rapidly than the temperature.

Thermodynamics.—If we call the volume of the substance in the liquid state v_1 and in the vapor state v_2 and if the volume occupied by it when partially vaporized is v , then

$$\frac{v - v_1}{v_2 - v_1} = m$$

is the fraction or proportion of the substance which has been vaporized, and

$$1 - m = \frac{v_2 - v}{v_2 - v_1}$$

is the fraction remaining in the liquid state. m as thus defined can have all values between 0 and 1, but has no meaning except when the two phases are coexistent, or in the area between the water and steam lines. We may solve for v , getting

$$v = (1 - m)v_1 + mv_2.$$

For convenience we may call the specific heat of the liquid at constant m , that is the amount of heat required to raise the temperature of unit amount one degree, keeping it at such a pressure that it is just

ready to vaporize, C_m , and similarly the specific heat of the vapor when just saturated H_m . The latent heat of vaporization we shall call L , that is, the amount of heat required to just vaporize the unit amount of liquid, keeping its temperature constant. All amounts of heat and energy we shall suppose measured in the same kind of units, for convenience.

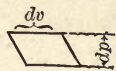


Fig. 10.

Consider now a small Carnot Cycle, of length dv and height dp . Its area is then the product $dpdv$, or substituting for dv and dp

$$dv = (v_2 - v_1) dm$$

$$dp = \frac{\partial p}{\partial T} dT;$$

the last equation being true since the pressure of the vapor depends upon the temperature only, we have for the area

$$dpdv = (v_2 - v_1) dm \frac{\partial p}{\partial T} dT.$$

Now this expression, the area of the cycle on the diagram of pressure and volume, is equal to the work done by the substance if caused to pass through this cycle. The heat absorbed by the substance in the expansion dv is entirely used in vaporizing the amount dm of the liquid and is hence equal to

$$Ldm.$$

Now it is easily shown, and is a fundamental truth of thermodynamics that the efficiency of a Carnot Cycle,

that is the ratio of the work done to the heat taken in at the upper temperature, is equal to the ratio of the range of temperature to the upper temperature. Applying this theorem to this case we have

$$\frac{(v_2 - v_1)dm \frac{\partial p}{\partial T} dT}{Ldm} = \frac{dT}{T},$$

whence

$$(29) \quad L = T(v_2 - v_1) \frac{\partial p}{\partial T}.$$

We can easily write the equations corresponding to those we have given for gases. For instance, the first law of thermodynamics becomes

$$(30) \quad \begin{aligned} dQ &= [(1 - m)C_m + mH_m]dT + Ldm \\ &= [m(H_m - C_m) + C_m]dT + Ldm. \end{aligned}$$

Special cases of interest are :

The isothermal expansion, $dT = 0$, $p = \text{const.}$

$$dQ = Ldm.$$

Expansion with m kept constant

$$dQ = [m(H_m - C_m) + C_m]dT.$$

Special cases :

$$m = 0, \text{ liquid state } \cdot dQ = C_m dT,$$

$$m = 1, \text{ vapor state } \cdot dQ = H_m dT.$$

Adiabatic Expansion and Entropy.—We may write the equation expressing the first law in the form

$$dQ = MdT + Ldm = TdS$$

where

$$M = m(H_m - C_m) + C_m.$$

Then

$$M = T \frac{\partial S}{\partial T},$$

$$L = T \frac{\partial S}{\partial m},$$

for inserting these values the equation becomes an identity.

Differentiating these partially by m and T respectively and taking their difference

$$\begin{aligned} \frac{\partial L}{\partial T} - \frac{\partial M}{\partial m} &= \frac{\partial S}{\partial m} + T \frac{\partial^2 S}{\partial m \partial T} - T \frac{\partial^2 S}{\partial m \partial T} \\ &= \frac{\partial S}{\partial m} = \frac{L}{T} \quad (\text{since } \frac{\partial T}{\partial m} = 0). \end{aligned}$$

But substituting the value of M

$$\begin{aligned} \frac{\partial M}{\partial m} &= H_m - C_m, \\ \frac{\partial L}{\partial T} - (H_m - C_m) &= \frac{L}{T} \end{aligned}$$

or

$$H_m - C_m = \frac{\partial L}{\partial T} - \frac{L}{T}.$$

Substituting this value the first law becomes

$$(31) \quad dQ = m \left(\frac{\partial L}{\partial T} - \frac{L}{T} \right) dT + C_m dT + L dm = T dS.$$

Then

$$dS = m \left(\frac{1}{T} \frac{\partial L}{\partial T} - \frac{L}{T^2} \right) dT + \frac{L}{T} dm + C_m \frac{dT}{T}$$

$$= d\left(\frac{mL}{T}\right) + C_m \frac{dT}{T},$$

and if C_m can be regarded as constant, which it probably is very nearly,

$$(32) \quad S = \frac{mL}{T} + C_m \log T + \text{const.}$$

and the equation of an adiabatic is

$$\frac{mL}{T} + C_m \log T = \text{const.}$$

To write these last equations in terms of p and v would require definite knowledge of the relation between T and p , a relation which is not easy to deduce on theo-

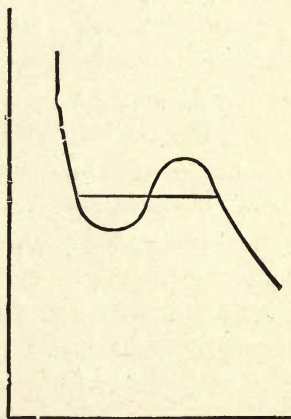


Fig. 11.

retical grounds, and does not yet appear to be easily and satisfactorily generalized from experimental data.

It was early suggested by Professor James Thomson,

brother of Lord Kelvin, that besides the actual forms of the isothermals, there might be an ideal form, which should not have the straight line nor the sharp bends of the form we have been discussing. The general form he suggested is shown in the diagram. The form of the surface or model would be different from that shown in Fig. 9, having at the left, over part of the area representing the change of state, a ridge, and to the right a deep hollow. A vertical section parallel to the axis of volume would have somewhat the same general shape as an isothermal, only reversed, showing with increasing volume the temperature first rising, then falling and then again rising. Points on the left side of the ridge, or the right side of the hollow might refer to states actually attainable; for instance, a liquid can be heated above its ordinary temperature of boiling without boiling at all, until finally it begins to do so almost explosively; this explosive action would seem to be the accompaniment of a passage from one state to the other, which might be represented by a passage from one portion of the surface to the other. The two isothermals as we have seen evidently do not belong to the same surface, the actual isothermal corresponding to the actual changing from the liquid to the vapor state by vaporization, a discontinuous process during which the substance is present in two phases, while the ideal isothermal corresponds to a continuous passage from one state to the other, a purely hypothetical process, during which the substance has only one phase. The points on the isothermal at which it slopes down from

left to right refer to conditions which may possibly be attainable when for instance a liquid is superheated, or a vapor undercooled; but the middle region, where the slope is upward, represents an unstable and explosive state, in which an increase of volume is accompanied by an increase of pressure. This may perhaps be regarded as the reason why the actual passage from one state to the other is discontinuous, each little part of the liquid, as it receives sufficient heat, passing suddenly and explosively to the vapor state, thus creating the two phases. One consideration of considerable importance can be stated; the fact that the amount of work a body can do during a closed cycle as the result of an amount of heat given to it is proportional to the range of temperature of the cycle leads to the corollary that no work can be done by an isothermal cycle. This might indeed be stated as one of the forms of the Second Law of Thermodynamics. If now a body of liquid be isothermally vaporized completely, and then at the same temperature caused to return to the original liquid state by the continuous process according to the ideal isothermal, then in the whole cycle no work is done, and hence algebraically the sum of all the areas on the plane of pressure and volume, which represents the work of the cycle, must be zero. The process is a purely hypothetical one, but the logic is conclusive, and we learn from it that the two areas enclosed between the two isothermals are equivalent. This relation we shall have occasion to make use of later. The fact that there is a critical point above

which the distinction between liquid and vapor ceases, and that a vapor may be made to pass from the gaseous to the liquid state continuously by compressing it at a temperature above the critical temperature, and then cooling it, carefully keeping its volume less than that at which it can begin to vaporize, seem to add significance to this idea of an ideal isothermal of continuous change of state.

CHAPTER VI.

EQUATION OF VAN DER WAALS.

So long as the actual bulk of all the molecules of a substance is negligible in comparison with the volume occupied by the substance, and so long as the mutual forces between the molecules only act for distances so short in comparison with the mean free paths of the molecules that the portions of their paths which are not straight are negligible in comparison with the straight portions, the substance will follow the laws of Boyle and Charles, and will be properly called an ideal gas, whether the molecules be smooth, hard spheres, or of less simple shapes, or even aggregations more or less complex, and whether the rebound be due to simple elastic forces on contact, or to forces acting as some power of the distance between the centers of the molecules. But no actual substances follow exactly the laws of Boyle and Charles, and hence the necessity of a theory more general. The equation of van der Waals, which we are about to discuss, is more general in two respects: first, it relieves us of the restriction that the volume of the molecules of the substance is negligible; second, it makes the assumption that there exist between the molecules forces of mutual attraction, which we may call cohesive forces. The second assumption is one which can evidently apply to liquids,

and it would appear that it must apply to gases also, since all known gases can be liquefied, and the same substance can exist at the same temperature and pressure side by side in the two phases of liquid and vapor. We can give this assumption more definite form by saying that besides the repulsive forces which act very strongly, but only at very small distances, each molecule of the substance, whether that substance be liquid or gas, exerts upon each other molecule of the same substance a force which falls off with the distance, but slowly enough so that at a considerable distance the force may be regarded as constant; then any molecule of the substance is subject to attractive forces exerted by molecules in all directions from it, which if it be well within the body of the substance are sensibly in equilibrium and cannot seriously affect its motion; but a molecule near the surface of this substance is subject to these forces on the side toward the body of the substance, but only to a very much less degree on the opposite side, the less as it approaches nearer the surface. If now the substance be restrained by the walls of the containing vessel, it is subject to two forces, one p , the pressure exerted by the walls themselves, which could be measured by a pressure guage, such as a column of mercury, the other, P , the cohesive force due to the mutual attraction of the molecules. The whole force acting upon the surface of the substance, which results in the returning to the interior of the substance of any molecules starting out toward the surface is the sum

$$p + P.$$

The form of the expression for the molecular pressure was deduced by van der Waals in the following manner: our lack of knowledge of the law of the forces between molecules would be a very serious matter if we were dealing with the motions of one molecule only, but as we are dealing with great numbers of them, we may be satisfied with average results; then on the average the force acting on any molecule near the surface tending to draw it back within the substance is proportional to the density of the substance, that is, to the number of attracting molecules, and the total force exerted upon a definite portion of the surface is again proportional to the number of molecules in it, that is, to the density of the substance, hence the total molecular pressure is proportional to the square of the density of the substance, or to the inverse square of the specific volume, that is

$$P = \frac{a}{v^2}.$$

The considerations which we have adduced in Chapter III. with regard to the effect upon the pressure of the volume of the molecules also apply here, and hence our equation takes the form

$$(33) \quad \left(p + \frac{a}{v^2} \right) (v - b) = \frac{1}{3} N m \bar{c}^2 = RT.$$

In our deduction so far we have carefully used the word substance, since everything we have said may be

equally well stated of either liquids or gases. In fact, van der Waals was led to this form of discussion by his study of the theories of capillarity and surface tension; so that it would seem to be a fair suggestion that this equation might apply both to the gaseous and to the liquid state. While this formula does not represent with perfect accuracy the behavior of actual gases, it may be regarded as a second approximation, much nearer the actual truth than the first approximation

$$(3) \quad pv = RT.$$

Other forms of this equation have been proposed, as that of Clausius,

$$\left(p + \frac{c}{T(v + \beta)^2} \right) (v - b) = RT,$$

or of Dieterici¹

$$\left(p + \frac{a}{v^2} \right) (v - b) = RT.$$

For the present, however, we shall confine our attention to van der Waals' form of the equation, and to that simply as describing the phenomena of a substance in the gaseous state. The more complete discussion of its properties we shall postpone to a later part of the chapter.

A gas satisfying this equation does not follow Boyle's Law. For we may write

¹ *Wied. Ann.*, 69, p. 685, 1899.

$$p = \frac{RT}{v - b} - \frac{a}{v^2},$$

$$pv = \frac{RT}{1 - \frac{b}{v}} - \frac{a}{v},$$

which is evidently not a constant. Whether the value of the product will be greater or less than RT , and whether it will increase or decrease with increasing volume depends upon the values of a and b , and can only be determined by experiment.

Experiments have been made on this point by Amagat, the results of which for air are shown by the accompanying diagrams, in which the abscissa represents not the volume but the pressure, and the ordinate the product, pv . The broken line represents the values computed by van der Waals¹ from his equation. The agreement is quite close, both curves showing a marked minimum in the value of pv . For hydrogen a may be taken as zero, giving

$$pv = \frac{RT}{1 - \frac{b}{v}},$$

which has no minimum point.

We may also find how nearly such a gas follows the laws of Charles and Gay Lussac. For an ideal gas the coefficients of change of pressure and of volume are the same and given by the formula

$$\alpha = \frac{1}{T_0},$$

¹ "Continuität," I., p. 106.

where T_0 is the standard temperature of melting ice, about 273° . For a gas following van der Waals' equa-

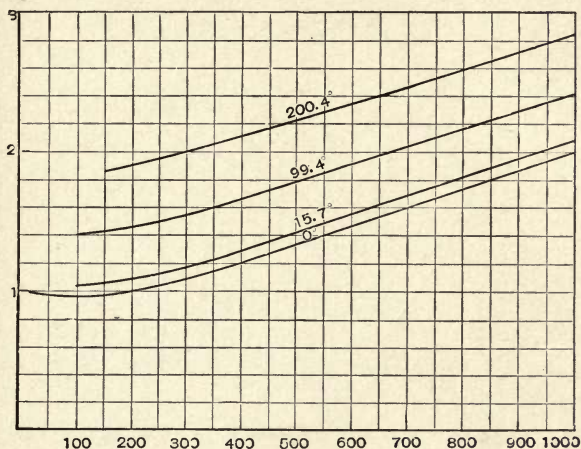


Fig. 12a.

tion, at the two temperatures T_1 and T_2 we may write for the pressures at the same volume

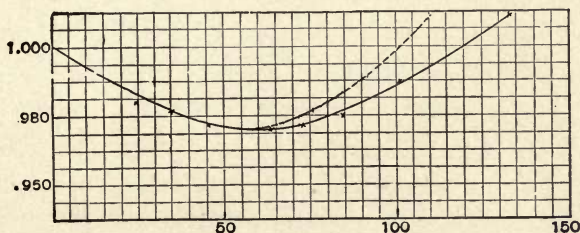


Fig. 12b.

$$p_1 = \frac{RT_1}{v - b} - \frac{a}{v^2},$$

$$p_2 = \frac{RT_2}{v-b} - \frac{a}{v^2},$$

$$p_2 - p_1 = \frac{R}{v-b}(T_2 - T_1)$$

$$\frac{p_2 - p_1}{T_2 - T_1} = \frac{R}{v-b}$$

That is, the rate of change of the pressure when the volume is kept constant and the temperature changes is constant, depending however on the volume. The coefficient is this rate divided by p_0 , the pressure at this volume and at the temperature T_0 , which is

$$p_0 = \frac{RT_0}{v-b} - \frac{a}{v^2},$$

$$\frac{p_2 - p_1}{T_2 - T_1} = \frac{R}{v-b} = \frac{p_0 + \frac{a}{v^2}}{T_0},$$

$$\alpha_p = \frac{p_2 - p_1}{p_0(T_2 - T_1)} = \frac{1}{T_0} \left(1 + \frac{a}{p_0 v^2} \right).$$

This pressure coefficient is a constant, but slightly larger than that for an ideal gas. It becomes identical with the latter for gas for which $a = 0$, as hydrogen, and approaches it very closely for an attenuated gas, for which v is very large.

The volume coefficient cannot be so simply determined, as its exact deduction involves the solution of a cubic equation, but a useful approximation applicable to the gaseous state can be made as follows:

Inasmuch as a/v^2 is a small correction, we may sub-

stitute in it for v its approximate value RT/p . We then have

$$\frac{a}{v^2} = \frac{ap^2}{R^2T^2},$$

$$\left(p + \frac{ap^2}{R^2T^2}\right)(v - b) = RT,$$

$$\begin{aligned} v - b &= \frac{RT}{p + \frac{ap^2}{R^2T^2}} = \frac{RT}{p} \frac{1}{1 + \frac{ap}{R^2T^2}} = \frac{RT}{p} \left(1 - \frac{ap}{R^2T^2}\right) \\ &= \frac{RT}{p} - \frac{a}{RT}. \end{aligned}$$

Differentiating by T , considering p constant

$$\frac{\partial v}{\partial T} = \frac{R}{p} + \frac{a}{RT^2} = \frac{R}{p} \left(1 + \frac{ap}{R^2T^2}\right).$$

but at the temperature T_0

$$v_0 - b = \frac{RT_0}{p \left(1 + \frac{ap}{R^2T_0^2}\right)},$$

$$v_0 = \frac{RT_0}{p \left(1 + \frac{ap}{R^2T_0^2}\right) \left(1 - \frac{b}{v_0}\right)},$$

hence

$$\alpha_v = \frac{1}{v_0} \frac{\partial v}{\partial T} = \frac{1}{T_0} \left(1 + \frac{ap}{R^2T^2}\right) \left(1 + \frac{ap}{R^2T_0^2}\right) \left(1 - \frac{b}{v_0}\right),$$

or approximately

$$\alpha_v = \frac{1}{T_0} \left(1 + \frac{ap}{R^2T^2} + \frac{ap}{R^2T_0^2} - \frac{b}{v_0}\right).$$

$$= \frac{1}{T_0} \left(1 + \frac{a}{pv^2} + \frac{a}{pv_0^2} - \frac{b}{v_0} \right).$$

At very high temperatures, when T is very large, this approaches the value

$$\begin{aligned} \alpha_{v(T \rightarrow \infty)} &= \frac{1}{T_0} \left(1 + \frac{ap}{R^2 T_0^2} - \frac{b}{v_0} \right) \\ &= \frac{1}{T_0} \left(1 + \frac{a}{pv_0^2} - \frac{b}{v_0} \right), \end{aligned}$$

which is a constant.

In the case of hydrogen, for which $a = 0$, our formula becomes

$$\alpha_v = \frac{1}{T_0} \left(1 - \frac{b}{v_0} \right).$$

We see that for a gas for which $a = 0$, whose equation is

$$p(v - b) = RT,$$

$$\alpha_v < \alpha_p.$$

This is actually the case with hydrogen, while all other gases have

$$\alpha_v > \alpha_p.$$

Thermodynamics.—In the case of a gas which follows van der Waal's equation we can no longer assume that the energy of the gas is independent of the volume, but if it expands at constant pressure, the amount of energy expended in the expansion is measured not by

$$\int p dv,$$

but by,

$$\int \left(p + \frac{a}{v^2} \right) dv.$$

But of this second integral only the first part represents work done by the gas upon outside bodies, the second part represents the increase of the potential energy of the gas. The first law of thermodynamics becomes then for such a gas

$$dQ = C_v dT + \left(p + \frac{a}{v^2} \right) dv,$$

in which evidently

$$C_v = \frac{\partial U}{\partial T}, \quad \frac{a}{v^2} = \frac{\partial U}{\partial v}.$$

This equation may also be written

$$(34) \quad dQ = C_v dT + \frac{RT}{v-b} dv,$$

a form which does not contain p at all. The other forms of the law, omitting either v or T , may be obtained by elimination with van der Waals' equation, and by the use of the approximations we employed in finding the coefficient of expansion.

$$(33) \quad \left(p + \frac{a}{v^2} \right) (v-b) = RT,$$

$$p(v-b) + \frac{a}{v} - \frac{ab}{v^2} = RT,$$

$$(v-b)dp + \left(p - \frac{a}{v^2} + \frac{2ab}{v^3} \right) dv = RdT,$$

omitting $2ab/v^3$ since both a and b are very small,

$$dv = \frac{RdT - (v-b)dp}{p - \frac{a}{v^2}}.$$

$$\frac{RT}{v-b} dv = \left(p + \frac{a}{v^2} \right) dv = \frac{p + \frac{a}{v^2}}{p - \frac{a}{v^2}} [RdT - (v-b)dp].$$

Putting as before

$$\frac{a}{v^2} = \frac{ap^2}{R^2 T^2},$$

$$\frac{p + \frac{a}{v^2}}{p - \frac{a}{v^2}} = 1 + \frac{2ap}{R^2 T^2},$$

$$\begin{aligned} \frac{p + \frac{a}{v^2}}{p - \frac{a}{v^2}} (v-b) &= \frac{p + \frac{a}{v^2}}{p - \frac{a}{v^2}} \cdot \frac{RT}{p + \frac{a}{v^2}} \\ &= \frac{RT}{p - \frac{ap^2}{R^2 T^2}} = \frac{RT}{p} \left(1 + \frac{ap}{R^2 T^2} \right), \end{aligned}$$

from which

$$\begin{aligned} \left(p + \frac{a}{v^2} \right) dv &= R \left(1 + \frac{2ap}{R^2 T^2} \right) dT \\ &\quad - \frac{RT}{p} \left(1 + \frac{ap}{R^2 T^2} \right) dp, \end{aligned}$$

and hence

$$dQ = \left[C_v + R \left(1 + \frac{2ap}{R^2 T^2} \right) \right] dT - \frac{RT}{p} \left(1 + \frac{ap}{R^2 T^2} \right) dp,$$

or putting .

$$(35) \quad C_v + R \left(1 + \frac{2ap}{R^2 T^2} \right) = C_p,$$

$$(36) \quad dQ = C_p dT - \frac{RT}{p} \left(1 + \frac{ap}{R^2 T^2} \right) dp.$$

Similarly we may eliminate T ,

$$dT = \frac{p - \frac{a}{v^2}}{R} dv + \frac{v - b}{R} dp,$$

$$\begin{aligned} dQ &= \frac{C_v}{R} (v - b) dp + \left[\frac{C_v}{R} \left(p - \frac{a}{v^2} \right) + \frac{RT}{v - b} \right] dv \\ &= \frac{C_v}{R} (v - b) dp + \left[\frac{C_v}{R} \left(p - \frac{a}{v^2} \right) + p + \frac{a}{v^2} \right] dv, \end{aligned}$$

which may be reduced to the form

$$(37) \quad dQ = \frac{C_v}{R} (v - b) dp + \frac{C_p}{R} \left(p - \frac{a}{v^2} \right) dv.$$

The entropy of such a gas is easily found, dividing both members of the equation

$$dQ = C_v dT + \frac{RT}{v - b} dv,$$

by T we have

$$\frac{dQ}{T} = dS = C_v \frac{dT}{T} + R \frac{dv}{v - b},$$

and integrating

$$(38) \quad S = C_v \log T + R \log (v - b) + \text{const.},$$

which is the same as the expression for the entropy of an ideal gas, with the co-volume, $v - b$, replacing the volume.

By the elimination of T the equation of an isentropic or adiabatic line is found to be

$$(39) \quad \left(p + \frac{a}{v^2}\right)(v - b)^{1 + \frac{R}{C_v}} = \text{const.},$$

which when a and b are both zero reduces to the familiar form for an ideal gas

$$(21) \quad pv^{\frac{C_p}{C_v}} = \text{const.}$$

Following is a tabulation of the principal equations relating to an ideal gas, and to one following van der Waals' equation.

IDEAL GAS.

$$(3) \quad pv = RT,$$

$$\alpha_p = \frac{1}{T_0},$$

$$\alpha_v = \frac{1}{T_0},$$

$$\frac{\partial U}{\partial v} = 0,$$

$$\frac{\partial U}{\partial T} = C_v,$$

$$(17) \quad C_p = C_v + R,$$

$$(21) \quad S = C_v \log T + R \log v + \text{Const.},$$

$$(20) \quad pv^{\frac{C_p}{C_v}} = \text{Const.},$$

$$dQ = C_v dT + \frac{RT}{v} dv,$$

$$dQ = C_p dT - \frac{RT}{p} dp,$$

$$(19) \quad dQ = \frac{C_p}{R} p dv + \frac{C_v}{R} v dp.$$

VAN DER WAALS'.

$$(33) \quad \left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

$$\alpha_p = \frac{1}{T_0} \left(1 + \frac{a}{p_0 v^2}\right),$$

$$\alpha_v = \frac{1}{T_0} \left(1 + \frac{ap}{R^2 T^2} + \frac{ap}{R^2 T_0^2} - \frac{b}{v_0}\right),$$

$$\frac{\partial U}{\partial v} = \frac{a}{v^2},$$

$$\frac{\partial U}{\partial T} = C_v,$$

$$(35) \quad C_p = C_v + R + 2 \frac{ap}{RT^2},$$

$$(38) \quad S = C_v \log T + R \log (v - b) + \text{Const.},$$

$$(39) \quad \left(p + \frac{a}{v^2}\right)(v - b)^{1 + \frac{R}{C_v}} = \text{Const.},$$

$$(34) \quad dQ = C_v dT + \frac{RT}{v - b} dv,$$

$$(36) \quad dQ = C_p dT - \frac{RT}{p} \left(1 + \frac{ap}{R^2 T^2}\right) dp,$$

$$(37) \quad dQ = \frac{C_p}{R} \left(p - \frac{a}{v^2}\right) dv + \frac{C_v}{R} (v - b) dp.$$

Ratio of Specific Heats. — From the discussion on p. 130 it would appear that for a gas which follows van

der Waals' equation the specific heat at constant pressure, C_p , includes not simply the heat necessary to increase the kinetic energy of the molecules, which we call C_v , and that necessary to do the external work accompanying the expansion but also the work necessary to increase the potential energy of the gas, due to the intermolecular attractions. This appears from the formula

$$(35) \quad \begin{aligned} C_p &= C_v + R \left(1 + \frac{2ap}{R^2 T^2} \right) \\ &= C_v + R \left(1 + \frac{2a}{pv^2} \right). \end{aligned}$$

Determinations¹ of the value of the ratio of the two specific heats are usually made by methods involving the adiabatic expansion or compression of a gas, as the method by the velocity of sound, or the change of pressure on sudden rarefaction or compression. Now the equation of an adiabatic, as we have seen, was

$$(39) \quad \left(p + \frac{a}{v^2} \right) (v - b)^{1 + \frac{R}{C_v}} = \text{Const};$$

hence the ratio determined is very nearly

$$\frac{C_p}{C_v} = 1 + \frac{R}{C_v},$$

although the effect of the term a/v^2 may be to increase it somewhat. But the true value of the ratio is shown by the equation above to be

$$\frac{C_p}{C_v} = 1 + \frac{R}{C_v} \left(1 + \frac{2a}{pv^2} \right).$$

¹ *Phys. Rev.*, XII., pp. 353-358, 1901.

In our deduction of this ratio in Chapter III., we took into account the energy of the rotational motions of the molecules, but not the work of overcoming the mutual attractions of the molecules. Introducing this element, the formula

$$\frac{C_p}{C_v} = 1 + \frac{2}{3} \frac{K}{H}$$

becomes

$$\frac{C_p}{C_v} = 1 + \frac{2}{3} \frac{K}{H} \left(1 + \frac{2a}{pv^2} \right).$$

This may help to account for the values of C_p/C_v , which were slightly higher than those indicated by the incomplete theory.

Form of Isothermals.—The equations of the isothermals of a substance following van der Waals' equation

$$(33) \quad \left(p + \frac{a}{v^2} \right) (v - b) = RT$$

are obtained by making T constant. It is convenient for the purpose of studying them to arrange the terms according to the powers of v . Clearing of fractions and multiplying up we have

$$pv^3 - pbv^2 + av - ab - RTv^2 = 0,$$

and arranging according to powers of v and dividing by the coefficient of v^3

$$v^3 - \left(\frac{RT}{p} + b \right) v^2 + \frac{a}{p} v - \frac{ab}{p} = 0.$$

This is an equation of the third degree in v , and as such has, according to the theory of equations, three

roots, which may, according to the values of p and T , be all real, or one real and two conjugate complex or imaginary quantities. In other words, a horizontal

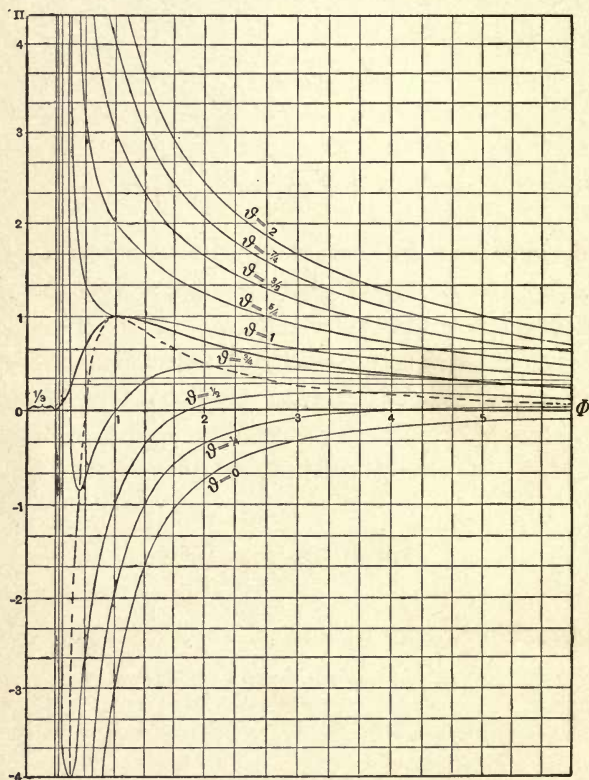


Fig. 13.

line, that is, a line of constant pressure, may cut the isothermal in one point or in three. Following out this suggestion we find that the isothermals of such a

substance have forms varying according to the temperature from very nearly those of an ideal gas to forms resembling those suggested by Professor James Thomson for a liquid and its vapor, shown in Fig. 11. From the considerations there adduced, we are able to draw some conclusions as to the relative position on these isothermals of the straight lines representing the actual transitions from the liquid to the vapor state. If we call the three roots of our equations, v_1 , v_2 , v_3 , then these are the abscissas of the three intersections of the isothermal by a line of constant pressure. This line of constant pressure will be the isothermal corresponding to the actual transformation at that temperature, if the area between it and the curved isothermal is algebraically zero, or the area under each, between the ordinates v_1 and v_3 , is the same, that is, calling the value of the constant pressure P

$$\int_{v_1}^{v_3} P dv = \int_{v_1}^{v_3} p dv.$$

Integrating the left side, and substituting for p its value

$$p = \frac{RT}{v-b} - \frac{a}{v^2},$$

$$\begin{aligned} P(v_3 - v_1) &= \int_{v_1}^{v_3} \frac{RT}{v-b} dv - \int_{v_1}^{v_3} \frac{a}{v^2} dv \\ &= RT \log \frac{v_3-b}{v_1-b} + a \left(\frac{1}{v_3} - \frac{1}{v_1} \right), \end{aligned}$$

or dividing by $(v_3 - v_1)$,

$$P = \frac{RT}{v_3 - v_1} \log \frac{v_3 - b}{v_1 - b} - \frac{a}{v_1 v_3}.$$

Further, the points P, v_1 , and P, v_3 , are on the curve and hence satisfy the equations

$$P = \frac{RT}{v_1 - b} - \frac{a}{v_1^2},$$

$$P = \frac{RT}{v_3 - b} - \frac{a}{v_3^2},$$

three equations which are sufficient to determine the corresponding values of P, v_1 , and v_3 , if we were able to solve them, as functions of T .

Critical Point.—By the theory of equations, if v_1, v_2, v_3 , are the three roots of the equation

$$v^3 - \left(\frac{RT}{p} + b \right) v^2 + \frac{a}{p} v - \frac{ab}{p} = 0.$$

Then

$$v_1 + v_2 + v_3 = \frac{RT}{p} + b,$$

$$v_1 v_2 + v_2 v_3 + v_3 v_1 = \frac{a}{p},$$

$$v_1 v_2 v_3 = \frac{ab}{p}.$$

Now at the critical point the horizontal actual isothermal vanishes, shortening until its two ends coincide, and hence at that point

$$v_1 = v_2 = v_3 = v_c.$$

If we then call the critical volume, pressure and temperature

$$v_c, p_c, T_c,$$

$$3v_c = b + \frac{RT_c}{p_c},$$

$$3v_c^2 = \frac{a}{p_c},$$

$$v_c^3 = \frac{ab}{p_c},$$

Solving we have

$$v_c = 3b,$$

$$p_c = \frac{1}{27} \frac{a}{b^2},$$

$$T_c = \frac{8}{27} \frac{a}{bR}.$$

That is, the properties of the critical state are completely determined by the constants a and b of the gas. The same results would have been obtained by defining the critical point as one at which the isothermal is horizontal and has a point of inflection, that is, the first and second derivatives vanish. Its coördinates then satisfy the three equations

$$p = \frac{RT}{v-b} - \frac{a}{v^2},$$

$$\frac{dp}{dv} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0,$$

$$\frac{d^2p}{dv^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0.$$

The solution of these equations will give the same values of the critical volume, pressure and temperature as before.

Corresponding States. — Let us introduce as a new set of variables the ratios between the actual and the critical volumes, pressures and temperatures which we may call the **reduced** volume, pressure and temperature and designate them by

$$(40) \quad \phi = \frac{v}{v_c} \quad \pi = \frac{p}{p_c} \quad \vartheta = \frac{T}{T_c}.$$

Then

$$v = \phi v_c = 3b\phi,$$

$$p = \pi p_c = \frac{1}{27} \frac{a}{b^2} \pi,$$

$$T = \vartheta T_c = \frac{8}{27} \frac{a}{bR} \vartheta.$$

Substituting these values in the original equation we have

$$\left(\frac{1}{27} \frac{a}{b^2} \phi + \frac{a}{9b^2\phi^2} \right) (3b\phi - b) = \frac{8}{27} \frac{aR}{b} \vartheta,$$

which reduces to the form

$$(41) \quad \left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 8\vartheta.$$

This is a purely numerical equation between the reduced volume, pressure and temperature, entirely independent of a , b or R . (Fig. 13 is plotted from this equation.) Two substances having the same values

of ϕ , π and ϑ are said to be in CORRESPONDING STATES, and we deduce from our equation the theorem for substances to which van der Waals' equation applies, that *if any two substances have temperatures and pressures bearing the same ratios to their critical temperatures and pressures, then their volumes will bear the same ratio to their critical volumes.* This is the theory of corresponding states, and may be further extended as follows: If we call the ratio of the vapor tension of a saturated vapor to the critical pressure

$$\Pi = \frac{P}{p_c},$$

substituting for P its value Πp_c , the equations for the reduced vapor tension are

$$\Pi = \frac{8}{3} \frac{\vartheta}{\phi_3 - \phi_1} \log \frac{3\phi_3 - 1}{3\phi_1 - 1} - \frac{3}{\phi_1 \phi_3},$$

$$\Pi = \frac{8\vartheta}{3\phi_1 - 1} - \frac{3}{\phi_1^2},$$

$$\Pi = \frac{8\vartheta}{3\phi_3 - 1} - \frac{3}{\phi_3^2}.$$

from which we conclude that Π , ϕ_1 , ϕ_3 , are related to ϑ by purely numerical equations, and hence two vapors at the same reduced temperatures have the same reduced pressures, and the reduced volumes of the liquid and saturated vapor are the same. Now all our quantitative statements regarding the critical phenomena and the theory of corresponding states have been expressly limited to substances following van der

Waals' equation. Experiment alone can tell whether the theory of corresponding states is more than an interesting bit of mathematical work. That it has some value is shown by so simple a case as the following, which we owe to van der Waals: The critical pressure for SO_2 is 78.9 atmospheres, and the critical temperature 428.4° (absolute), those of ether 36.9 and 463° respectively. For SO_2 at the temperature 412.9° the vapor tension is 60 atmospheres. Then

$$\Pi = \frac{60}{78.9} = .7605 \quad \vartheta = \frac{412.9}{428.4} = .964.$$

For ether at the same reduced pressure, the absolute pressure is

$$P = \Pi p_c = .7605 \times 36.9 = 28.4,$$

and according to Sajotschewski this pressure corresponds to an absolute temperature of 445.8° , whose reduced value would be

$$\frac{445.8}{463} = .963,$$

which is in close enough agreement with the value .964 for SO_2 . The most complete test has been made by S. Young in a series of experiments which space does not permit us to reproduce entire. He made comparisons of quite a number of substances, the names and critical data of some of which are given in the following table:

CRITICAL DATA.

Substance.	Formula.	Mol. Wt.	T_0	p_c	v_c
Fluor-benzol,	$C_6H_5.F$	95.8	559.55	33,912	2.822
Chlor-benzol,	$C_6H_5.Cl$	112.2	633.00	33,912	2.731
Brom-benzol,	$C_6H_5.Br$	156.6	670.00	33,912	2.056
Iodo-benzol,	$C_6H_5.I$	203.4	721.00	33,912	1.713
Benzol,	C_6H_6	77.84	561.50	36,395	3.293
Carbon tetrachloride,	CCl_4	153.45	556.15	34,180	1.799
Stannic chloride,	$SnCl_4$	259.3	591.70	28,080	1.347
Ether,	$(C_2H_5)_2O$	73.84	467.40	27,060	3.801
Methyl alcohol,	$CH_3.OH$	31.93	513.00	59,760	3.697
Ethyl alcohol,	$C_2H_5.OH$	45.90	516.10	47,850	3.636
Propyl alcohol,	$C_3H_7.OH$	59.87	536.70	38,120	3.634
Acetic acid,	$CH_3.CO_2H$	59.86	594.60	43,400	2.846

In this table p_c is given in millimeters of mercury. The values for the critical volumes are not observed directly, but extrapolated for the critical temperature in accordance with the rule of Cailletet and Mathias that the arithmetic mean of the densities of the liquid and saturated vapor is a linear function of the temperature.

The following tables contain some of the results of Young's work, embodied in a comparison between the behavior of fluor-benzol and the other substances investigated. The subscript 0 will refer to fluor-benzol. When the reduced pressures were the same, that is, $\Pi/\Pi_0 = 1$, the ratios of the other reduced co-ordinates were found to vary as follows, subscript 1 referring to the liquid state and 3 to the saturated vapor:

Substance.	ϑ/ϑ_0		ϕ_3/ϕ_{03}		ϕ_1/ϕ_{01}	
	from	to	from	to	from	to
C_6H_5Cl		1.1309		1.137		1.1246
C_6H_5Br		1.1976		1.189		1.1802
C_6H_5I		1.2885		1.282		1.2772
C_6H_6	0.9890	1.0035		0.946		0.9439
CCl_4	0.9699	0.9939	0.969	1.017	1.0173	1.0248
$SnCl_4$	1.0679	1.0575		2.282	1.2700	1.2910
$(C_2H_5)_2O$	0.8431	0.8353		1.035	1.0319	1.0456
CH_3OH	1.0127	0.9168	0.533	0.473	0.4317	0.4172
C_2H_5OH	1.0494	0.9223	0.706	0.625	0.6307	0.6058
C_3H_7OH	1.0997	0.9592	0.903	0.836	0.8198	0.7937
CH_3COOH	1.1278	1.0626	0.545	0.631		0.6342

When the reduced temperatures were the same, that is, $\vartheta/\vartheta_0 = 1$, the ratios of the other reduced coördinates were found to vary as follows:

Substance.	π/π_0		ϕ_3/ϕ_{03}		ϕ_1/ϕ_{01}	
	from	to	from	to	from	to
C_6H_5Cl	0.998	1.007		1.139		1.1245
C_6H_5Br	0.987	1.007		1.194		1.1800
C_6H_5I	0.985	1.007		1.286		1.2773
C_6H_6	1.338	1.073	0.842	0.940		0.9479
CCl_4	1.460	1.008	0.828	1.401		1.0266
$SnCl_4$	0.706	0.828	1.336	1.262	1.2657	1.2913
$(C_2H_5)_2O$	0.705	0.798	1.101	1.025	1.0284	1.0983
CH_3OH	0.359	1.762	1.244	0.484		0.409
C_2H_5OH	0.201	1.411	2.076	0.648	0.6044	0.5900
C_3H_7OH	0.099	1.124	2.678	0.866		0.772
CH_3COOH	0.476	1.280	0.894	0.631		0.623

In these tables the behavior of closely allied substances shows in general a satisfactory agreement with the theory of corresponding states, as shown both by the narrow limits between which the values lie, and the nearness of these ratios to unity, but substances

of widely different types, such as alcohols and their derivatives, show marked and systematic variations, hence while in its qualitative form this theory may apply to bodies of similar constitution, it is evident that it cannot apply without further explanation or amplification to bodies of diverse constitution.

Another method of discussion was also suggested by Mr. Young, which has been carried into more detail in an interesting paper on the critical state by Dieterici.¹ In the equation

$$3v_c = b + \frac{RT_c}{p_c},$$

substituting for b its value $v_c/3$ we have

$$3v_c = \frac{v_c}{3} + \frac{RT_c}{p_c},$$

$$\frac{RT_c}{v_c p_c} = \frac{8}{3}.$$

Now RT_c/p_c is the volume which an ideal gas would have at the critical pressure and temperature, which we may call the ideal critical volume, and indicate by v_k . Then for a gas following van der Waals' equation

$$\frac{v_k}{v_c} = \frac{8}{3},$$

or the ideal critical volume is $\frac{8}{3}$ of the actual critical volume. A table is given collecting the results of the

¹ *Wied. Ann.*, 69, pp. 685-705, 1899.

determinations of Ramsey and Young which bear upon this point. The ratio is in no case $\frac{8}{3}$, that is 2.667, but for the benzol derivatives and some others has values very nearly 3.75, for a considerable list of esters the values lie close to 3.8, for ethyl and propyl alcohol, 4.02, while the values for methyl alcohol, 4.52, and acetic acid, 5.00, are entirely different. Something the same range of values is found by collating the results of other workers for different substances, as found in original papers and Landolt and Börnstein's tables. The direct determination of the critical volume is a matter of considerable difficulty, and the tendency of the systematic errors to be expected is to give its value too small, and hence the ratio of the ideal to the actual critical volume too large. Taking these facts into consideration, the declaration of Mr. Young seems to be substantiated that for all substances which can attain the critical state without chemical change, this ratio is very nearly the same, being not far from 3.7. As has been shown the equation

$$(33) \quad \left(p + \frac{a}{v^2}\right)(v - b) = RT$$

leads to the value 2.667. Other formulæ have been proposed which suggest the possibility of closer approximation by the increased number of constants available, as

$$p = RT \cdot \frac{1}{v} \left[1 + \frac{b}{v} + a_1 \left(\frac{b}{v}\right)^2 + a_2 \left(\frac{b}{v}\right)^3 + \dots \right] - P,$$

where P may be of the form a/v_2 , but these, on investigation lead to values of our ratio

$$\frac{v'_k}{v_c} \leq 3.0,$$

of which the results from van der Waals' original form are a special case. Dieterici proposes the following entirely empirical formula, which is of a form not unlike that of van der Waals; if we put the "molecular pressure" equal to $a/v^{\frac{5}{3}}$ our equation becomes

$$(42) \quad \left(p + \frac{a}{v^{\frac{5}{3}}}\right)(v - b) = RT.$$

Multiplying up and arranging according to the powers of v

$$v^{\frac{8}{3}} - \left(b + \frac{RT}{p}\right)v^{\frac{5}{3}} + \frac{a}{p}v - \frac{ab}{p} = 0.$$

We may introduce the new variable $x = v^{\frac{1}{3}}$ and write our equation symbolically

$$f(x) = x^8 - \alpha x^5 + \beta x^3 - \gamma = 0.$$

This equation is of the eighth degree, but can according to the theory of equations have at most three real positive roots. It has also one negative root and four imaginary ones. At the critical point the three positive roots coincide and we have

$$f(x) = x^8 - \alpha x^5 + \beta x^3 - \gamma = 0,$$

$$f'(x) = 8x^7 - 5\alpha x^4 + 3\beta x^2 = 0,$$

$$f''(x) = 56x^6 - 20\alpha x^3 + 6\beta x = 0.$$

Solving these three equations for α , β and γ , we have

$$\alpha = 4x^3, \quad \beta = 4x^5, \quad \gamma = x^8,$$

or introducing the values of α , β and γ , and calling the critical volume, pressure, and temperature as before v_c , p_c , T_c ,

$$b + \frac{RT_c}{p_c} = 4v_c,$$

$$\frac{a}{p_c} = 4v_c^{\frac{5}{3}},$$

$$\frac{ab}{p_c} = v_c^{\frac{8}{3}},$$

whose solutions are

$$a = 4p_c v_c^{\frac{5}{3}},$$

$$b = \frac{v_c}{4},$$

or

$$v_c = 4b,$$

$$p_c = \frac{a}{4(4b)^{\frac{5}{3}}},$$

$$T_c = \frac{15ab}{4(4b)^{\frac{5}{3}}R},$$

equations which are entirely analogous to, though of slightly different form from those of van der Waals for the critical constants. Substituting the values of a and b in

$$(42) \quad \left(p + \frac{a}{v^3}\right)(v - b) = RT$$

we have

$$\left(p + \frac{4p_c v_c^{\frac{5}{3}}}{v^{\frac{5}{3}}}\right) \left(v - \frac{v_c}{4}\right) = RT,$$

$$\left(\frac{p}{p_c} + \frac{4}{(v/v_c)^{\frac{5}{3}}}\right) \left(\frac{v}{v_c} - \frac{1}{4}\right) = \frac{RT}{p_c v_c} = \frac{15}{16} \frac{RT}{RT_c},$$

or introducing the reduced volume, pressure and temperature

$$(43) \quad \left(\pi + \frac{4}{\phi^{\frac{5}{3}}}\right) \left(\phi - \frac{1}{4}\right) = \frac{15}{16} \vartheta.$$

From the foregoing it is apparent that this equation has the same general properties as the form due to van der Waals, including the theory of corresponding states, which depends upon the fact that the equation relating the reduced pressure, volume and temperature is purely numerical. Still further, in the equation

$$b + \frac{RT_c}{p_c} = 4v_c$$

putting for b its value $v_c/4$ and for RT_c/p_c as before v_k

$$\frac{v_k}{v_c} = 3.75.$$

This value corresponds very closely to that found by Mr. Young from his experiments.

Dieterici even goes farther, and deduces from theoretical considerations a formula connecting the pressure, volume and temperature of the form¹

$$(44) \quad p = \frac{RT}{v - b} \cdot e^{-\frac{a}{RTv}},$$

¹ See Chapter VII., p. 171.

and since for the critical point $dp/dv=0$ and $d^2p/dv^2=0$, he is able to find the value of the ratio of the ideal to the actual critical volume, which proves to be

$$\frac{v_k}{v_c} = 3.695.$$

Berthelot¹ has shown that the actual isothermal for carbon dioxide through its critical point agrees almost exactly with that given by van der Waals' equation, taking the constants of the latter from the coördinates of the critical point, for pressures greater than the critical pressure, that is, in the region near the liquid state, while for smaller pressures and the vapor state the actual isothermal follows very closely that given by a special form of Clausius' equation,

$$\left[p + \frac{a}{(v + 3b)^2} \right] (v - b) = RT,$$

or in reduced coördinates

$$\left[\pi + \frac{16}{3} \frac{1}{(\phi + \frac{1}{3})^2} \right] (\phi - \frac{1}{9}) = \frac{32}{9} \vartheta,$$

while an equation can be found giving a curve very nearly agreeing with the actual isothermal by writing for a/v^2 ,

$$\frac{a}{v^2 + 2lvb + mb^2},$$

which gives a reduced equation of the form

$$\left(\pi + \frac{1}{3} \frac{13^3}{108\phi^2 + 96\phi - 35} \right) (\phi - \frac{1}{3}) = \frac{32}{9} \vartheta.$$

¹ *Comptes Rendus*, 130, pp. 69 and 115, 1900.

He finds further that van der Waals' equation gives for liquids isothermals of the same general shape as the actual ones, but very differently situated. Attempting to introduce some form of correction which should make the two isothermals coincide, he finds this is best done by regarding b as a function of the temperature. The empirical form

$$b_T = b_e \left[1 + .3 \left(\frac{T}{T_e} - 1 \right) \right]$$

obtained from the study of the isothermals of liquid carbon dioxide, which leads to the reduced equation

$$\left(\pi + \frac{3}{\phi^2} \right) (3\phi - .7 - .3\vartheta) = 8\vartheta,$$

gives isothermals almost identical with those for carbon disulphide and ethyl chloride at 0° C. He concludes from this that the equation of van der Waals, if the volume b be regarded as dependent upon the temperature, represents satisfactorily the behavior of normal liquids. The objections which have been raised against it are due largely, he believes, to the fact that our experimental study has naturally been more of vapors under their relatively smaller pressures than of liquids with their relatively larger pressures.

CHAPTER VII.

VAPORIZATION.

THE study of the motions of the molecules of a liquid may be approached in three not entirely dissimilar ways. Equations of the type of that of van der Waals appear to apply to the liquid as well as to the gaseous state, both because of the resemblance between the forms of their isothermal curves and those found from experiments, and because the conditions underlying the assumptions which lead to these equations are even more characteristic of liquids than of gases. A second method of approaching the study of the liquid state is by giving attention to the phenomena of change of state, while a third consists in the direct attack upon the problem of the motion of molecules, the mean distance between which is of the order of their dimensions.

The first method has been pursued with some success by Traube¹ of the Technische Hochschule, Berlin. He distinguishes carefully between the volume of the substance of the atoms which make up the molecule, the volume of the molecule, which may be due not only to the bulk of the atoms, but also to their arrangement, and the "co-volume," the space not occupied by the molecules, in which the individual

¹ *Wied. Ann.*, 61, pp. 380-400, 1897.

molecule is free to move. This co-volume is the $v - b$ of the generalized formula

$$(45) \quad (p + P)(v - b) = RT.$$

In the case of a liquid the external pressure p is so small in comparison with the "molecular pressure" that it may be disregarded, and calling the co-volume Φ the equation becomes

$$(46) \quad P\Phi = RT,$$

that is, the product of the molecular pressure by the co-volume of a liquid is proportional to the absolute pressure. While this result is interesting, it can only be verified by experiments which shall give us values of both P and Φ for a variety of substances in the liquid states. The volume of a gram molecule of a gas at 0° C. and 76 cm. pressure is 22,380 c.c., a figure which may also be regarded as representing the co-volume. For normal liquids, that is those in which the molecules contain the number of atoms called for by their formulæ, Traube finds, by deriving the volume of the molecules from determinations of refractive indices, that for the same pressure and temperature the co-volume of a gram-molecule is very nearly 24.5 c.c., and hence that the molecular pressure for such liquids is $22,380/24.5 = 913$ atmospheres. This value is not very different from that found by Nernst for carbon dioxide from the formula $P = a/v^2$ which is 970 atmospheres.¹ The complete verification of this form

¹ Nernst, "Theoretical Chemistry," Trans. by Palmer, p. 196.

of the theory would seem to depend upon experimental determinations of P . It may be that experiments upon the thermal expansion and coefficients of compressibility of liquids will furnish the necessary data.

Equilibrium Between Liquid and Vapor.—The second method is well summarized by Dieterici¹ whose treatment we shall follow. Any demonstration which may be given for the purpose of establishing the Maxwell distribution of the velocities of the molecules of a gas depends fundamentally upon the assumption that the number of the molecules is exceedingly great, and that a knowledge of the speed and direction of one molecule, or of any number, gives no clue as to the speed or direction of any other molecule. Hence we can believe that this distribution is just as applicable to and just as probable for the motion of the molecules of liquids as of gases.² The attractive forces between the molecules, as we have indicated in the last chapter, cannot particularly influence the motion of the molecules except near the surface. Let us suppose then that we have a substance present in both the liquid and vapor form, with the surface of separation horizontal. We may suppose further, for the sake of simplicity, that each follows the laws of ideal gases, except near their surfaces, and that each exhibits Maxwell's distribution of velocities. While we may speak of the plane of separation of the two phases, they are really separated not by a plane, but by a non-homo-

¹ *Wied. Ann.*, 66, pp. 826–858, 1898.

² Rayleigh, *Phil. Mag.* (5), 49, p. 1900.

geneous layer. If the line O represents the position of the mathematical surface of separation, then below it we may consider a plane to be passed, which we represent by B , at a sufficient distance so that all the liquid below B can be regarded as completely homogeneous, while in the space between B and O a molecule as it approaches O is subject to stronger and stronger forces tending to draw it back toward the

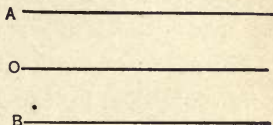


Fig. 14.

body of the liquid. Similarly we may pass a plane A above O , at such a distance that above A the vapor will be homogeneous, while only between O and A will it be non-homogeneous, being denser near O on account of the attraction of the molecules of the liquid. Only the vertical components of the motions of the molecules tend to carry them from one of the regions into the other, hence our discussion is restricted to the vertical components of the velocities, which we shall designate by the letter u . We shall indicate quantities referring to the region of vapor generally by the subscript a and those referring to the liquid state by the subscript b , the constants of Maxwell's formula being α and β respectively. Then the number of molecules in the unit volume of the liquid having the vertical components of their velocities between u and $u + du$ is

$$\frac{n_b}{\beta\sqrt{\pi}} e^{-\frac{u^2}{\beta^2}} du$$

and in the unit volume of the vapor similarly

$$\frac{n_a}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} du.$$

If as a first approximation we assume that both phases of the substance follow the laws of ideal gases, the number of such molecules striking a unit area of the surface B in one second will be the first of these numbers multiplied by the speed u , that is,

$$\frac{n_b}{\beta\sqrt{\pi}} e^{-\frac{u^2}{\beta^2}} u du.$$

Now of all the molecules which strike the surface B from below, a part only go some distance into the non-homogeneous layer, and then return on account of the strong unbalanced force they meet there, while some go clear through beyond the plane A into the region of vapor. In general, disregarding for the present the effects of collisions, molecules having the vertical components of their velocities greater than a certain minimum value which we may call s will be capable of passing up entirely through the non-homogeneous layer into the region of vapor; these we may call briefly the "capable" molecules; while molecules having the vertical component less than this amount will penetrate to a greater or less distance into the space between B and A , and then return to the liquid. Then the total number of molecules which will pass in one second through a unit area of the surface B into the region of vapor will be the sum total of all

the molecules the vertical component of whose velocities is greater than s , or calling this number n_s ,

$$n_s = \int_s^\infty \frac{n_b}{\beta\sqrt{\pi}} e^{-\frac{u^2}{\beta^2}} u \, du.$$

This expression is readily integrated by putting $\frac{u}{\beta} = x$, giving

$$\begin{aligned} n_s &= \frac{n_b}{\beta\sqrt{\pi}} \int_s^\infty e^{-\frac{u^2}{\beta^2}} u \, du = \frac{n_b\beta}{\sqrt{\pi}} \int_{s/\beta}^\infty e^{-x^2} x \, dx \\ &= \frac{n_b\beta}{\sqrt{\pi}} \left[-\frac{1}{2} e^{-x^2} \right]_{s/\beta}^\infty = \frac{n_b\beta}{2\sqrt{\pi}} e^{-\frac{s^2}{\beta^2}}. \end{aligned}$$

The same reasoning shows that the number of molecules of the vapor having the vertical components of their velocities between u and $u + du$ which strike unit area of the surface A from above in one second is

$$\frac{n_a}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} u \, du.$$

Now, barring mutual collisions, there is nothing to prevent any molecules passing down through A from passing completely into the liquid, or rather, on account of the attraction of the liquid they must inevitably pass down into it, hence the total number of molecules passing down through unit area of A in one second and entering the liquid is

$$\int_0^\infty \frac{n_a}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} u \, du = \frac{n_a\alpha}{2\sqrt{\pi}}.$$

and when a state of equilibrium is attained this must be the same as n_s , the number passing from the liquid to the vapor or

$$n_s = \frac{n_a \alpha}{2\sqrt{\pi}} = \frac{n_b \beta}{2\sqrt{\pi}} e^{-\frac{s^2}{\beta^2}}.$$

Hence the condition of equilibrium that equal numbers of molecules pass into and out of the liquid in the same time gives us the relation

$$n_a \alpha = n_b \beta e^{-\frac{s^2}{\beta^2}}.$$

We shall next consider the amount of energy which the molecules carry with them in their passage into and out of the liquid. We shall assume that the mass of the molecules is the same in both states, that is, that there is no dissociation or association of the molecules accompanying the change of state. Each molecule having the vertical component of its velocity equal to u has associated with that component the energy $\frac{1}{2}mu^2$. Then the total energy of the molecules having components between u and $u + du$ which pass up through a unit area of B in a second is

$$\frac{1}{2}mu^2 \frac{n_b}{\beta\sqrt{\pi}} e^{-\frac{u^2}{\beta^2}} u du,$$

and the molecules which pass through this unit area in a second into the region of vapor carry with them a total energy

$$\int_0^\infty \frac{1}{2}mu^2 \frac{n_b}{\beta\sqrt{\pi}} e^{-\frac{u^2}{\beta^2}} u du = \frac{n_b m}{2\beta\sqrt{\pi}} \int_0^\infty e^{-\frac{u^2}{\beta^2}} u^3 du.$$

This integral is easily evaluated by the same substitution as before and by application of formula (8) of p. 27, giving

$$\begin{aligned} \frac{n_b m \beta^3}{2 \sqrt{\pi}} \int_{s/\beta}^{\infty} e^{-x^2} x^3 dx \\ = \frac{n_b m \beta^3}{2 \sqrt{\pi}} \left\{ \left[-\frac{1}{2} x^2 e^{-x^2} \right]_{s/\beta}^{\infty} + \int_{s/\beta}^{\infty} e^{-x^2} x dx \right\} \\ = \frac{n_b m \beta^3}{2 \sqrt{\pi}} \left[\frac{1}{2} \frac{s^2}{\beta^2} e^{-\frac{s^2}{\beta^2}} + \frac{1}{2} \cdot e^{-\frac{s^2}{\beta^2}} \right] \end{aligned}$$

which reduces, after writing n_s for its value, to the form

$$n_s \left(\frac{1}{2} m s^2 + \frac{1}{2} m \beta^2 \right).$$

This then is the amount of energy taken out of the liquid by the n_s molecules leaving it. Now consider a molecule the vertical component of whose velocity is exactly s ; such a molecule would have associated with this motion the energy $\frac{1}{2} m s^2$; having exactly the speed s it would just barely penetrate through A to the homogeneous region arriving there without motion and without energy. The energy $\frac{1}{2} m s^2$ which it has lost, then represents exactly the work which the molecule must do in overcoming the attraction of the mass of liquid and penetrating through the non-homogeneous layers between B and A . The remainder, $\frac{1}{2} n_s m \beta^2$ then represents the energy which the capable molecules bring with them into the vapor region. Similarly the molecules passing down from the vapor into the liquid carry with them the energy

$$\frac{n_a m}{2\alpha\sqrt{\pi}} \int_0^\infty e^{-\frac{u^2}{\alpha^2}} u^3 du$$

which is easily shown to be equal to

$$\frac{n_a m \alpha^3}{2\sqrt{\pi}} \cdot \frac{1}{2} = \frac{1}{2} n_a m \alpha^2$$

and the condition of equilibrium that equal amounts of energy shall be associated with the molecules passing into and out of the vapor gives us the condition

$$\frac{1}{2} n_a m \alpha^2 = \frac{1}{2} n_b m \beta^2$$

$$\alpha = \beta$$

That is, the most probable speeds of the molecules of the liquid and vapor states, and hence their average speed, and their mean kinetic energy of translation are the same. Knowing that their temperatures must be the same this is a result that might reasonably have been expected. Introducing this into the relation between n_a and n_b we have

$$n_a = n_b e^{-\frac{s^2}{\alpha^2}},$$

that is, since n_a and n_b are proportional to the densities of the vapor and liquid states respectively, the ratio of these densities is equal to e^{-s^2/α^2} where s is the speed necessary to penetrate the non-homogeneous layer, and α the most probable speed of the molecules.

We have next to consider the momenta associated with the molecules of the liquid and vapor phases of the substance. This momentum carried by the molecules is proportional to the internal pressures. The

sum of all the momenta brought from below to a unit area of the surface B in one second is

$$\int_0^{\infty} mu \cdot \frac{n_b}{\beta V \pi} e^{-\frac{u^2}{\beta^2}} u du = \frac{n_b m}{\beta V \pi} \int_0^{\infty} e^{-\frac{u^2}{\beta^2}} u^2 du,$$

but of this amount only that associated with molecules having u at least as great as s can ever pass through the surface A to the region of vapor, and this momentum is

$$\frac{n_b m}{\beta V \pi} \int_s^{\infty} e^{-\frac{u^2}{\beta^2}} u^2 du,$$

which may be reduced by the methods previously employed to the form

$$\frac{n_b m \beta^2}{2V \pi} \left[\frac{s}{\beta} e^{-\frac{s^2}{\beta^2}} + \int_{s/\beta}^{\infty} e^{-x^2} dx \right],$$

of which the integration of the last term is affected only by development in series or by the use of tables. But not all this momentum which the capable molecules carry with them through the surface B is also carried with them through the surface A , but only that which is associated with the excess of this component of the velocity over the critical speed s . This is conditioned by the energy relation for any molecule which passes through the non-homogeneous layer,

$$\frac{1}{2} m u_b^2 - \frac{1}{2} m u_a^2 = \frac{1}{2} m s^2,$$

consequently the total momentum passing upward through unit area of the surface A is

$$\int_s^\infty m \sqrt{u^2 - s^2} \frac{n_b}{\beta \sqrt{\pi}} e^{-\frac{u^2}{\beta^2}} u \, du,$$

which is again an exceedingly difficult form to integrate. We may however attempt a different method of treatment. If the energy of all the molecules associated with the $+u$ motion could suddenly be decreased by the uniform amount $\frac{1}{2}ms^2$, then immediately after this change the law of distribution of u would be

$$\frac{n_b}{\beta \sqrt{\pi}} e^{-\frac{u^2 + s^2}{\beta^2}} du.$$

Now the effect of the forces acting in the non-homogeneous layer is exactly the same as if they were able to impress upon each of the capable molecules such a negative velocity as should serve to decrease its energy by $\frac{1}{2}ms^2$, and hence to produce in them just such a distribution of velocities as is indicated by the above form of Maxwell's law, where u will refer to the actual component velocities possessed by the molecules on reaching the surface A . Then the sum of the momenta which the capable molecules will carry through unit area of A in one second is¹

$$\int_0^\infty mu \frac{n_b}{\beta \sqrt{\pi}} e^{-\frac{u^2 + s^2}{\beta^2}} u \, du = \frac{n_b m e^{-\frac{s^2}{\beta^2}}}{\beta \sqrt{\pi}} \int_0^\infty e^{-\frac{u^2}{\beta^2}} u^2 \, du,$$

which may be shown by the methods of p. 27 to be equal to

¹This same method might have been applied to the study of the passage of masses and energy through the surface A , leading to the same results as those we have obtained.

$$\frac{n_b m \beta^2 e^{-\frac{s^2}{\beta^2}}}{4\pi} = \frac{n_s}{2\sqrt{\pi}} m \beta.$$

The sum of the momenta carried down through unit area of the surface A is similarly

$$\begin{aligned} & \int_0^\infty m u \frac{n_a}{\alpha \sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} u \, du \\ &= \frac{n_a m}{\alpha \sqrt{\pi}} \int_0^\infty e^{-\frac{u^2}{\alpha^2}} u^2 \, du \\ &= \frac{n_a m \alpha^2}{4\pi} = \frac{n_s}{2\sqrt{\pi}} m \alpha. \end{aligned}$$

Hence the two relations which we have already deduced that

$$n_s = \frac{n_b \beta}{2\sqrt{\pi}} e^{-\frac{s^2}{\beta^2}} = \frac{n_a \alpha}{2\sqrt{\pi}},$$

and that

$$\alpha = \beta,$$

and hence

$$n_a = n_b e^{-\frac{s^2}{\beta^2}},$$

satisfy not only the conditions that in a state of equilibrium the masses passing through the surface A in the two directions, and the kinetic energies associated with them are equal, but also that the momenta associated with them, and hence the external pressures are equal.

A careful review of the three problems we have just studied shows that the three equations which we

have obtained as indicating equilibrium of mass or number of molecules, of energy, and of momenta are, omitting common constant factors

$$n_a \alpha = n_b \beta e^{-\frac{\epsilon^2}{\beta^2}},$$

$$n_a \alpha^3 = n_b \beta^3 e^{-\frac{\epsilon^2}{\beta^2}},$$

$$n_a \alpha^2 = n_b \beta^2 e^{-\frac{\epsilon^2}{\beta^2}}.$$

The inevitable conclusion from these different equations is that $\alpha = \beta$, and that the meaning of this is, not simply that some energy associated with the motions of the molecules in the liquid state is equal to a corresponding energy in the gaseous state, but that the mean kinetic energy of translation is the same in both states, but not necessarily the total energy of the molecules. This condition makes the condition of thermal equilibrium between liquid and vapor definite and the same as that between two gases. This conclusion may otherwise be stated that the mean kinetic energy of translation of the molecules is the measure of the temperature in liquids as in gases, or

$$\frac{1}{3} N m \overline{c^2} = RT.$$

Review of Assumptions. — In the foregoing discussion we have assumed that the Maxwell distribution of velocities holds equally well for the molecules of liquids and gases, that the mass of the molecules is the same in both states, and that the volumes of

the molecules can be entirely disregarded. Of these assumptions the first we believe to be valid, and the second we regard as consistent with the facts in a great many cases; the discussion of the consequences of any deviation from this assumption can well be deferred. The third assumption has two immediate consequences; we have disregarded the effect of the volume occupied by the molecules upon the number of molecules which will pass through any area in a given time, and we have entirely ignored the possibility of mutual collisions. If we apply to this case the results of the discussion in Chapter III. of the effect of the volume of the molecules when this is small, but not negligibly small in comparison with the volume of the gas or liquid, if the volume occupied by a number N of the molecules of the substance in the vapor state is v_a , and in the liquid state, v_b , we have to consider as the number of molecules per unit volume, not the number per unit total volume, N/v_a or N/v_b , but the number per unit of *co-volume*, that is

$$n_a = \frac{N}{v_a - b_a},$$

$$n_b = \frac{N}{v_b - b_b},$$

and hence

$$\frac{n_a}{n_b} = e^{-\frac{s^2}{\beta^2}} = \frac{v_b - b_b}{v_a - b_a},$$

or

$$\frac{v_a - b_a}{v_b - b_b} = e^{\frac{s^2}{\beta^2}},$$

and we have, not the ratio of the densities, or of the specific volumes in the two states, but of the co-volumes determining the relation between s and the actual speeds of the molecules.

In ignoring the possibility of collisions between the molecules we have assumed that the particular molecules whose conditions we considered at the surface B passed right up through the non-homogeneous layer into the region of vapor above A ; but in reality all this region between A and B is filled with either the liquid or the vapor in very dense form, so that almost never could a molecule pass up directly, but it is much more likely to strike other molecules, and by the impact transmit upward its energy and momentum, and keep intact the number of molecules traveling upward. This will not affect our conclusions with regard to the equilibrium between the number of molecules passing through the layer in both directions, nor with regard to the equilibrium in the state of momentum, or of pressure, but will compel us to rediscuss the problem of the energy relations.

The energy of the capable molecules passing up through unit area of B in one second was shown to be

$$n_s(\frac{1}{2}ms^2 + \frac{1}{2}m\beta^2)$$

and our interpretation was perfectly general; that $\frac{1}{2}ms^2$, being the energy of a molecule just exactly capable of penetrating the non-homogeneous layer was the work that must be done by each molecule against the cohesive forces of the liquid, while $\frac{1}{2}n_s m\beta^2$

was the energy associated with the vertical component of the velocities of the n_s molecules after penetrating this layer. An obvious interpretation is that $\frac{1}{2}n_s ms^2$ represents the latent heat of vaporization, measured in dynamical units, but attempts to verify this suggestion by reference to numerical data lead to such inconsistencies and confusion that we prefer to seek for a different interpretation, rather than fill our pages with a statement of what cannot be. So far we have drawn all conclusions from considerations of equilibrium, but the value of the latent heat of vaporization is to be found not by a study of conditions of equilibrium, but of the amount of energy required to change a definite quantity of the substance from the liquid to the vapor state. Disregarding for the present changes in the energy of the internal motion of the molecules, which might give a corrective term, this energy is equal to the work which must be done against all the forces, whether cohesive or of external pressure, in the expansion of the liquid to the gas. Now we have shown in Chapter III., p. 69 that the total of these forces is

$$\frac{1}{3}nm\bar{c}^2\left(1 + \frac{b}{v}\right) = \frac{RT}{v-b},$$

hence the work in a small expansion dv is

$$\frac{RT}{v-b}dv,$$

and the total work in expanding from the liquid to the vapor state is

$$RT \int_{v_b}^{v_a} \frac{dv}{v-b},$$

which, if we assume that b is the same for both the liquid and the vapor states, becomes

$$RT \log \frac{v_a - b}{v_b - b}.$$

If we substitute for $(v_a - b)/(v_b - b)$ its value e^{s^2/β^2} and remember that

$$RT = \frac{1}{3} N m \bar{c}^2,$$

and that

$$\bar{c}^2 = \frac{3}{2} \beta^2,$$

this expression reduces to the form

$$RT \log \frac{v_a - b}{v_b - b} = RT \frac{s^2}{\beta^2} = \frac{1}{2} N m s^2,$$

which is the same as the value we have just obtained from conditions of equilibrium. But in considering the transmission of energy through the non-homogeneous layer, we have to take into account still another effect of the volume of the molecules. The intermolecular forces which have their effect in the non-homogeneous region act not upon the energy of the molecules, but simply on the molecules themselves, the carriers of the energy; consequently, while any molecule is progressing through this layer upward, it is doing work against these forces, but whenever it comes into collision with another molecule it transmits its energy a certain distance, in the case of a central collision just equal to the diameter of the molecule, without loss because unaffected by these intermolecular forces. The expression which we have just

deduced represents the loss of kinetic energy as the *energy* is transmitted through this non-homogeneous layer. But, in the process of vaporization of a liquid molecules actually pass out of the liquid region into the vapor region, while the non-homogeneous layer, even if not composed of the same identical molecules, remains intact. Hence we may regard the molecules as actually passing from the inner homogeneous region to the outer homogeneous region, and hence doing an amount of work which is greater than that which we have just found in the ratio of $v/v - b$. The latent heat will then be ¹

$$(47) \quad L = RT \int_{v_b}^{v_a} \frac{v dv}{(v - b)^2} \\ = RT \left[\log \frac{v_a - b}{v_b - b} + \frac{b}{v_b - b} - \frac{b}{v_a - b} \right].$$

The generalized form of van der Waals' equation applying to the two phases is

$(p + P_b)(v_b - b) = (p + P_a)(v_a - b) = \frac{1}{3}Nmc^2 = RT$,
where P_a and P_b are the molecular pressures within the vapor and the liquid respectively. Substituting from these equations we have

$$L = RT \log \frac{v_a - b}{v_b - b} + (P_b - P_a)b,$$

or

$$(48) \quad L = RT \log \frac{p + P_b}{p + P_a} + (P_b - P_a)b.$$

¹ Milner, *Phil. Mag.* (5), 43, pp. 291-304, 1897.

Since this expression contains only the work which is done against the forces acting in the non-homogeneous layer, and not the work done against the external pressure, in pushing back the containing wall, as each part of the gas, fully expanded, comes out of the non-homogeneous layer, we must add to it the work done against the external pressure,

$$p(v_a - v_b) = P_b(v_b - b) - P_a(v_a - b),$$

giving

$$L = RT \log \frac{v_a - b}{v_b - b} + P_b v_b - P_a v_a.$$

We have already shown that the first term of this result for the latent heat of vaporization is the same as the value we have previously found for the loss of the kinetic energy of the molecules in passing through the non-homogeneous layer. The second term is the product of the molecular pressure in the liquid state by the volume of the liquid, and may be called the potential energy of the liquid film, or non-homogeneous layer. It is equal to the work which would be done in displacing the film by an amount equal to the volume of the liquid, against the molecular pressure which holds it extended. This is what actually occurs in the vaporization of the liquid. The third term is a similar expression for the vapor state, but of much smaller amount; the difference between the two potential energies represents then the amount of work which must be done in vaporizing a body of liquid, in addition to that necessary to replace the loss of kinetic

energy of the molecules as they pass through the surface layer.

The method of this chapter may be applied to the deduction of the equation of the vapor or of the liquid. The pressure exerted upon the walls of the containing vessel by a vapor or liquid depends upon the sum of the impulses of the molecules that actually strike the wall. To reach the wall the molecules have to pass through a non-homogeneous layer in which forces act which tend to retard the approach of the molecules to the wall. The expression for the pressure may then be written

$$p = \frac{RT}{v-b} e^{-\frac{s^2}{\beta^2}},$$

where s is the speed which a molecule must have in order to just penetrate to the wall. This may also be written

$$p = \frac{RT}{v-b} e^{-\frac{A}{RT}},$$

where A is an amount of energy proportional to the work of a molecule in overcoming the cohesive forces in reaching the wall. If we assume that this quantity A is proportional to the density, we may write

$$A = \frac{a}{v},$$

where a is constant, and

$$(44) \quad p = \frac{RT}{v-b} e^{-\frac{a}{RTv}}.$$

The condition that for the critical state the first and second derivatives of p by v vanish gives us

$$\frac{a}{RT_c v_c^2} = \frac{1}{v_c - b},$$

$$\frac{2a}{RT_c v_c^3} = \frac{1}{(v_c - b)^2},$$

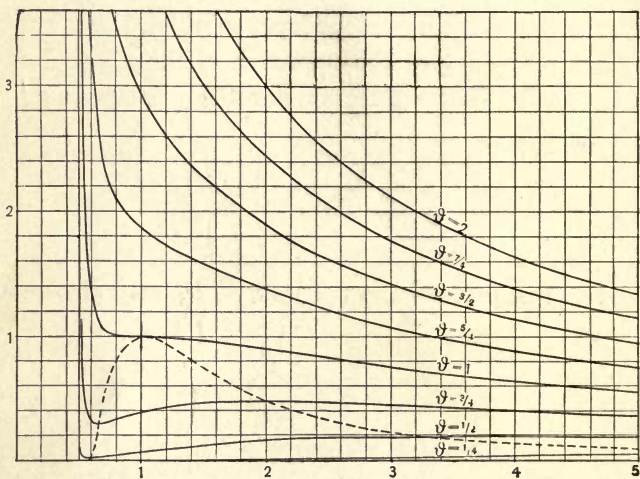


Fig. 15.

$$\frac{2}{v_c} = \frac{1}{v_c - b}, \quad b = \frac{1}{2}v_c,$$

$$\frac{a}{RT_c v_c} = 2,$$

$$p_c = \frac{RT_c}{v_c - b} e^{-\frac{a}{RT_c v_c}} = \frac{RT_c}{v_c} \cdot 2e^{-2},$$

$$\frac{RT_c}{p_c v_c} = \frac{v_k}{v_c} = \frac{1}{2} e^2 = 3.695,$$

which is almost exactly the mean value found by Young, while the equation between the reduced coördinates is

$$\pi = \frac{1}{2} e^2 \frac{\vartheta}{\phi - \frac{1}{2}} e^{-\frac{2}{\vartheta \phi}},$$

$$(49) \quad \pi = \frac{\vartheta}{2\phi - 1} e^{2 - \frac{2}{\vartheta \phi}}.$$

If, however, in the equation

$$(44) \quad p = \frac{RT}{v - b} e^{-\frac{a}{RTv}}$$

we assume that a/RTv is small, we may write for $e^{-a/RTv}$ the first two terms of its development, $1 - a/RTv$, giving

$$p = \frac{RT}{v - b} - \frac{a}{v(v - b)},$$

or disregarding b in the last term as small,

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

which is van der Waals' equation, so that at fairly high temperatures or for fairly large volumes the equations are practically identical, a and b having the same meaning, though they give entirely different values of the critical constants.

CHAPTER VIII.

MOLECULES WITHIN A LIQUID.

IN Chapters VI. and VII. we discussed formulæ of the form

$$(45) \quad (p + P)(v - b) = RT,$$

of which van der Waals' equation was a special case, and showed that they could be applied to the study of liquids, and to the phenomena of vaporization, as well as to gases.

That the special equations like those of van der Waals, Clausius, and others could completely describe the behavior of liquids was not to be expected because they were deduced on the assumption that the free paths of the molecules, while not necessarily infinitely greater than the dimensions of the molecules, were still much larger, and that the chances for collisions of more than two molecules at a time were so small that they could be left entirely out of the account. According to van der Waals equation, the volume in the liquid state must necessarily be less than the critical volume $3b$, b itself being, as we have found, only 4 times the volume occupied by the molecules themselves. From this we see that if the space were divided up evenly among all the molecules, each one could have a cubical space whose volume could not exceed 12 times the volume of the molecule itself, that

is, $12 \times \frac{1}{6}\pi\sigma^3 = 2\pi\sigma^3$ and whose edge consequently could not exceed $\sigma\sqrt[3]{2\pi}$, and hence must be considerably less than twice the diameter of the molecule. It is evident also that as the result of an indefinite increase of pressure, external or internal, the limiting volume of the liquid would be not b but the smallest space into which the molecules could be packed, which, if the molecules were spherical would be a little more than $\frac{1}{4}b$, approximately $\frac{1}{3}b$.

There is evidence also that while in most gases the composition of the molecules is usually represented fairly accurately by the ordinary formulæ, in many if not most liquids the molecules are more complex, being made up of two or more of the simple gas-molecules united, and hence are both larger and less numerous, so that even if the same equations applied the numerical constants must be different, while the latent heat of vaporization, so called, must include also some latent heat of dissociation. This cause of variation will be taken up in Chapter XI.

While we have then a fairly satisfactory discussion of the relations of pressure, covolume, temperature and kinetic energy of the molecules of a liquid, and of the phenomena of vaporization, we still have to discuss the motions of the molecule within the liquid, and find if possible its mean free path.

Mean Free Path. — We shall first assume, as in the case of gases, that the molecules are all spherical, of diameter σ , and that all but the one we are especially considering are at rest. But because the molecules

are so near together we shall assume a particular distribution, such that the centers of adjacent molecules are situated at the vertices of equilateral triangles. This arrangement gives the smallest volume when all the molecules are in contact, giving a total volume of about $\frac{1}{3}b$, as we have just stated, or $\frac{1}{9}$ of the critical

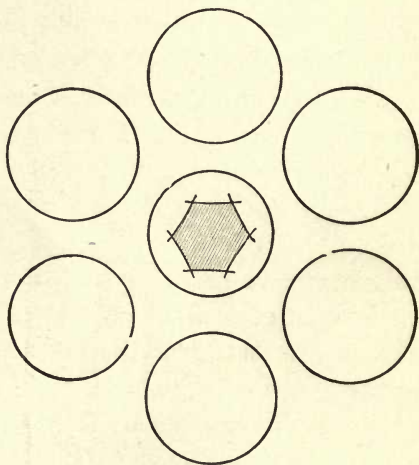


Fig. 16.

volume, hence the distance between the centers of adjacent molecules cannot exceed $\sigma\sqrt[3]{9}$, and hence will usually be considerably less than 2σ . Fig. 16¹ will represent a section through the centers of seven such molecules. Consider the molecule in the middle as the one to be studied, and about the others describe spheres with radius σ . These spheres will intersect,

¹ Jäger, *Wien. Ber.*, 102, p. 257.

since the distance between centers is less than 2σ , leaving a small volume represented by the shaded space in the figure, about the center of the moving molecule. This small volume is the region in which the center of the molecule is free to move, and in which we must find its mean path. We can for our purposes consider this space spherical, of radius h , (Fig. 17). Our problem is now to find the average length of the path from any point of the surface of

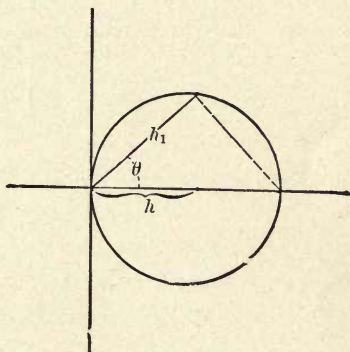


Fig. 17.

this spherical space to any other point of it, that is, to find the average value of the line h_1 , making the angle ϑ with the diameter of the sphere. We have found previously (p. 34, Eq. (15)) that the proportion of such lines making an angle between ϑ and $\vartheta + d\vartheta$ is $\sin \vartheta d\vartheta$ while the length of such a line is evidently $2h \cos \vartheta$, hence the average value will be

$$\int_0^{\pi/2} 2h \cos \vartheta \sin \vartheta d\vartheta = h [\sin^2 \vartheta]_0^{\pi/2} = h.$$

This value, being based upon the assumption that all the molecules except the one were at rest, has still to be multiplied by the ratio \bar{c}/\bar{r} , which we call as before $\frac{3}{4}$, giving

$$l = \frac{3}{4}h.$$

We still have to find the value of h , which evidently cannot vary much from the radius of the sphere described in the free space about the center of the moving molecule. This last easily appears to be $d - \sigma$ where d represents the mean distance between the centers of adjacent molecules.

We may find the value of d by the following device : Suppose the space v , which contains N molecules, to be rectangular in shape ; along one edge the molecules are placed regularly at intervals d from center to center ;

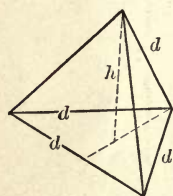


Fig. 18.

suppose the number in the row to be n_1 . Then a second row of n_1 molecules is placed so that the centers of three adjacent molecules will be at the vertices of an equilateral triangle of edge d . The distance between the lines of centers will be

the altitude of this triangle, which is $\frac{1}{2}d\sqrt{3}$. Suppose there can be placed in all n_2 such rows. Then above this layer place another layer, so that each molecule will have its center at the same distance d from the centers of the three nearest molecules of the lower layer, the four centers being thus at the vertices of a regular tetrahedron whose edge is d ,

and whose altitude must be $\frac{1}{3}d\sqrt{6}$. Suppose the total number of such layers in the space to be n_3 . Then the total volume will be

$$n_1 d \cdot n_2 \cdot \frac{1}{2} d \sqrt{3} \cdot n_3 \cdot \frac{1}{3} d \sqrt{6} = n_1 n_2 n_3 d^3 \cdot \frac{1}{2} \sqrt{2} ,$$

but this volume is v ; and $n_1 n_2 n_3$ is the total number of molecules, N , hence

$$v = \frac{1}{2} \sqrt{2} N d^3 ,$$

$$d^3 = \sqrt{2} \frac{v}{N} .$$

The minimum volume, which we may call b_1 , is found by letting $d = \sigma$,

$$b_1 = \frac{1}{2} \sqrt{2} N \sigma^3 ,$$

from which

$$\frac{\sigma^3}{d^3} = \frac{b_1}{v} , \quad \frac{\sigma}{d} = \sqrt[3]{\frac{b_1}{v}} .$$

Substituting, we have

$$l = \frac{3}{4}(d - \sigma) = \frac{3}{4}d \left(1 - \frac{\sigma}{d} \right) = \frac{3}{4}d \left(1 - \sqrt[3]{\frac{b_1}{v}} \right) .$$

The space actually occupied by the molecules is (p. 69)

$$N \cdot \frac{1}{6} \pi \sigma^3 = \frac{\sqrt{2} \pi b_1}{6} = .735 b_1 .$$

This was according to the deduction of van der Waals' equation $\frac{1}{4}b$, and hence $\frac{1}{12}$ the critical volume, from which we find

$$b_1 = .339b .$$

The greatest possible value of d , and hence of l , would be for the critical state, in which $v_c = 3b$, and hence

$$\frac{\sigma^3}{d^3} = \frac{b_1}{v_c} = \frac{.339b}{3b} = .113,$$

$$d = \sigma \sqrt[3]{\frac{1}{.113}} = 2.07\sigma,$$

$$l = \frac{3}{4}(2.07\sigma - \sigma) = .8\sigma.$$

For $v = 2b$ which is for van der Waals' equation a fair average value of the volume, and which for Dieterici's equation, which we have found to agree remarkably well with some of the properties of the critical state, is the critical volume, we have

$$\frac{b_1}{v} = \frac{.339b}{2b} = .169.$$

$$d = 1.64\sigma,$$

$$l = .48\sigma.$$

From these we conclude that the critical volume is not more than 9 (or 6) times the minimum attainable volume, that the mean distance between the centers of adjacent molecules can only in the extreme case exceed twice their diameters, but is ordinarily much less; that the mean free path is less, usually less than half this diameter, having of course for its minimum value 0 when the molecules are in contact, and $d = \sigma$.

Pressure.—The average number of impacts per second of such a moving molecule is evidently c/l . Suppose one particular molecule moving in its free space with the speed c , making c/l impacts per second

and having a momentum of mc ; then the total force required to hold it in this space will be the product mc^2/l . The area on which this force is exerted is the area of the little spherical space of radius h and area $4\pi h^2$, so that the pressure will be $mc^2/4\pi h^2 l$. Passing to averages, and expressing the total pressure by $p + P$ we have

$$p + P = \frac{\overline{mc^2}}{4\pi h^2 l},$$

or substituting for l its value $\frac{3}{4}h$,

$$p + P = \frac{\overline{mc^2}}{3\pi h^3}.$$

Multiplying by $\pi N h^3$ we have

$$(p + P) \pi N h^3 = \frac{1}{3} N \overline{mc^2},$$

which is of the form

$$(p + P) \Phi = \frac{1}{3} N \overline{mc^2} = RT$$

given in Chapter VII. It readily appears that the sum of all the free spaces of volume $\frac{4}{3}\pi h^3$ about each of the N molecules is $\frac{4}{3}\pi N h^3$, and hence that the *covolume* $\pi N h^3$ is $\frac{3}{4}$ of the sum of these free spaces, the factor $\frac{3}{4}$ being the ratio \bar{c}/\bar{r} , used in finding the mean free path. It is evident from the previous discussion that h cannot except in the extreme case of the critical volume exceed $\frac{1}{2}d$, and hence that this covolume $\pi N h^3$ cannot exceed $\frac{1}{8}\pi N d^3 = \sqrt{2}/8\pi v = .57v$, that is, the covolume is ordinarily less than half the volume of the

liquid, usually much less, *e. g.*, if $v = 2b$, $\frac{2}{3}$ the critical volume or for Dieterici's equation the critical volume, the covolume is $.27v$, about $\frac{1}{4}$. This gives the covolume a physical meaning, although its analytical form is different from that given by van der Waals' equation, $v - b$, in which b is a constant. Eliminating h by the equations

$$h = d - \sigma = d \left(1 - \frac{\sigma}{d} \right),$$

$$d^3 = \sqrt[3]{2} \frac{v}{N},$$

we get

$$(p + P) \sqrt[3]{2} \pi v \left(1 - \frac{\sigma}{d} \right)^3 = \frac{1}{3} N m \bar{c}^2 = RT$$

or

$$(p + P) \sqrt[3]{2} \pi v \left(1 - \sqrt[3]{\frac{b_1}{v}} \right)^3 = \frac{1}{3} N m \bar{c}^2 = RT,$$

which is expressed explicitly in terms of the volume of the liquid and the space occupied by the molecules.

For Dieterici's equation the critical volume is $2b$, and hence, as we have found above, d cannot exceed 1.642σ , l cannot be greater than $.482\sigma$, and Φ cannot be greater than $.27v$, so that a substance following Dieterici's equation in the gaseous state ought to have its behavior in the liquid state in close harmony with the results of the present discussion.

Internal Pressure. — Approximate values of the internal pressure of liquids have been given in Chapter VII. Some of these were based upon assumptions as to the covolume of the liquid which we did not

there attempt to verify ; others were obtained by the use of the formula a/v^2 , which can hardly apply in this state, although its form was derived from a study of the theory of surface tension and capillarity. Their approximate agreement would nevertheless seem to indicate that we have at least learned the order of magnitude of this pressure. The formula deduced for the latent heat might also be used, if only we could readily find the covolume in the liquid state.

Since this internal pressure is but the equilibrant of the forces at the surface, which determine the volume of the liquid and manifest themselves in the phenomena of surface tension, it must have the same temperature coefficient, and hence can be expressed by the formula $P = P_0(1 - \epsilon t)$ in which P_0 represents the value of P at 0°C. , and ϵ is the temperature coefficient of surface tension. Since ϵ is always positive it appears that with rising temperature the internal pressure, but not the total pressure, decreases. Our general equation of condition may similarly be written, neglecting the external pressure,

$$P\Phi = \frac{1}{3}N\overline{mc_0^2}(1 + \alpha t).$$

Dividing this by the last we get

$$\Phi = \frac{\frac{1}{3}N\overline{mc_0^2}(1 + \alpha t)}{P_0(1 - \epsilon t)},$$

which shows, since α and ϵ are both positive, that Φ must increase rapidly with the temperature.

The coefficient of compressibility is defined as the ratio of the relative decrease of volume to the pressure producing the decrease. Analytically it is

$$\kappa = -\frac{1}{v} \frac{\partial v}{\partial p},$$

differentiating the equation

$$(p + P)\sqrt[3]{2\pi v} \left(1 - \sqrt[3]{\frac{b_1}{v}}\right)^3 = RT,$$

on the assumption that T is constant, we obtain, after simplification

$$\kappa = -\frac{1}{v} \frac{\partial v}{\partial p} = \frac{1 - \sqrt[3]{\frac{b_1}{v}}}{p + P} = \frac{\Phi}{(p + P)\sqrt[3]{2\pi v}},$$

or dropping p and solving for P ,

$$P = \frac{1}{\kappa} \frac{\Phi}{\sqrt[3]{2\pi v}},$$

which still requires a knowledge of Φ or of the ratio

$$\frac{\Phi}{\sqrt[3]{2\pi v}} = \left(1 - \frac{\sigma}{d}\right)^3$$

to find P . The minimum values for σ/d , and the maximum values for κ which would give a lower limit for P , would of course be found in the critical state, for which $(1 - \sigma/d)^3$ can easily be determined.

Approximate numerical results might perhaps be obtained by computing the covolume in terms of v and b_1 , determining the latter by finding the minimum volume to which the liquid could be compressed by the most intense pressure which could be applied.

CHAPTER IX.

SOLUTIONS.

MIXTURES and solutions may, like pure substances, exist in either the gaseous, the liquid, or the solid state. The elementary laws of mixtures of gases which do not react chemically with each other have already been developed (Chap. II., pp. 38-43). When equilibrium is attained the mean kinetic energy of translation of the molecules is the same for each of the gases composing the mixture, and most of the other properties are additive; for instance the pressure exerted is the sum of all the pressures that would be exerted by the different gases if each were present separately, occupying the whole volume, and the energy is the sum of the energies of all the component gases. In general we may say that gases and vapors mix in all proportions, and the equations representing the behavior of the mixtures are of the same type as those referring to pure substances. The question arises with regard to the entropy of a mixture of gases, whether it is to be regarded as the sum of the entropies of the different components each regarded as occupying all the volume with its appropriate partial pressure; or regarded as occupying their proportional parts of the volume, with a pressure equal to that of the mixture. This latter view is evidently the

correct one in the case of successive additions of portions of a single gas, as after the volumes are brought into contact with each other diffusion takes place spontaneously without the expenditure of energy or the absorption of heat; while allowing each portion to fill the whole available space, the addition of each successive increment will demand the expenditure of energy, in compressing both the portion of gas already present, and that being added, and hence there will result a change either of the temperature or of

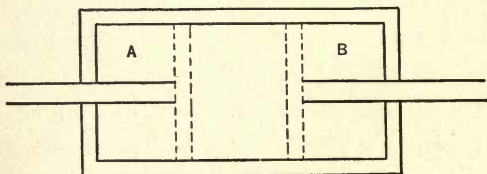


Fig. 19.

the entropy. Suppose, however, two different gases at the same pressure and temperature are placed in contact and allowed to diffuse into each other; this process can take place without expenditure of energy and without absorption of heat, but we can also imagine the diffusion to take place by a method which will involve the expenditure of work, and hence, if the temperature be kept constant, with an absorption of heat and a change in the entropy. Suppose that in a cylinder we have two gases, which we will call *A* and *B*, and two movable pistons, one of which, say the one to the left, will allow the gas *A* to pass

through it freely, while it is perfectly impervious to the gas B . Similarly the one to the right we may consider permeable to the gas B , but impervious to A . We shall consider the two pistons to be originally in contact with each other, with the gas A to the left and B to the right, the positions of the pistons being so chosen that the two gases are at the same pressure. Now the piston at the left, being perfectly permeable to the gas A experiences when at rest no excess of force from A tending to move it in either direction, while the gas B , passing through the other piston, exerts its full pressure upon it, hence there is a tendency for this piston to be pushed by the gas B to the extreme left hand end of the cylinder, doing upon it an amount of work just the same as if the gas A were not present and hence, if the temperature be kept constant, absorbing an amount of heat just equivalent to this work. Similarly the gas A will tend to push the piston at the right to the extreme right hand end of the cylinder, doing upon it, if the temperature be kept constant, the amount of work it would do in the same isothermal expansion of the gas B were not present, and absorbing the corresponding amount of heat. When both these processes have been accomplished the diffusion is complete, but each amount of gas has, during the diffusion, absorbed at constant temperature a certain amount of heat, and hence changed its entropy by a certain amount. It is easy to see that for each gas this change is just the same as that which would take place if it were al-

lowed to expand from its original volume and the pressure of the mixture of gases to the full volume of the mixture and the partial pressure which it there exerts. The entropy of a substance depends only upon its state, hence we conclude that the entropy of a mixture of gases is the sum of the entropies which each would have if occupying the whole volume of the mixture at its appropriate partial pressure. This method of treatment evidently cannot be applied to different portions of the same gas so that our previous conclusion will still hold, that the entropy of a large body of a single gas is the sum of the entropies of the smaller volumes of which it is made up, each at the pressure of the whole. The process which we have just considered is an ideal one. The transformation we have described is evidently reversible, hence no objections to it can be raised on that score. Its validity then depends upon the possibility of being able to realize such pistons which shall be permeable to one gas, but not to another. We know that hot palladium allows hydrogen to pass through it with considerable freedom, while ammonia gas, on account of its great solubility in water, will pass with considerable freedom through a wet membrane, hence such a system might be realized for these two gases. Since we believe in the uniformity of the laws of nature we then accept this theorem as general.

The study of solid solutions, such as alloys, mixed crystals, etc., and of the phenomena of diffusion in solids, has attracted much attention in recent years,

and has yielded some results of value, but is beyond the scope of this work.

Liquid solutions may be classified according to the state of the components either before the solution, or when they have been separated. Thus we speak of solutions of a gas, of a liquid, or of a solid. The simplest case of a liquid solution is one in which one component is so much more volatile than the other that the vapor above the solution may be regarded as a pure vapor. This may be done when the dissolved substance is a gas, in which case the vapor of the solvent is disregarded, or when the dissolved substance is a non-volatile liquid or solid, in which case the vapor of the solvent only is considered.

Absorption of Gases. — The amount of a gas which a given liquid can dissolve has been found by experiment to be proportional to the pressure of the gas upon the surface of the liquid; or in other words, the quantity of the gas contained in a given volume of the liquid bears a definite ratio to the quantity contained in the same volume of the free space above it which is independent of the pressure and depends at any given temperature only upon the liquid and gas concerned. This statement, which is commonly known as HENRY'S LAW, expresses with reasonable accuracy the behavior of many gases; it is not strictly true in all cases, however, and hence is to be regarded, like Boyle's Law, as a convenient and useful first approximation. The difference in the solubilities of different gases is shown by the following values of the coef-

ficient of absorption, that is the ratio of the volume of the gas absorbed to the volume of the absorbing substance, selected from data given by Bunsen.¹

Substance.		Solvent.	
		Water.	Alcohol.
Ammonia,	NH ₃	727.2	
Sulphur dioxide,	SO ₂	43.56	144.55
Sulphuretted hydrogen,	H ₂ S	3.233	9.54
Nitrous oxide,	N ₂ O	.778	3.268
Carbon dioxide,	CO ₂	1.002	3.2
Carbon monoxide,	CO	.0243	.2044
Oxygen,	O ₂	.03	.284
Nitrogen,	N ₂	.0145	.1214
Air,		.0179	
Hydrogen,	H ₂	.0193	.0673

It is readily seen that gases which are more strongly absorbed by one liquid are in general also more strongly absorbed by the other liquid, but there seems to be no simple and universal law relating the different solubilities.

As has been stated, Henry's law is to be regarded as simply a first approximation. That the coefficient of absorption should be independent of the pressure could be reasonably expected in the case of the less soluble gases for moderate pressures. That this is true is shown by the following tables² for the absorption of carbon dioxide in water, in which the column marked p gives the pressure in mm. of mercury and α the coefficient of absorption:

¹ For a more complete discussion, with reference to the literature on the subject and tabulations of the results see Winkelmann, "Handbuch der Physik," I., pp. 669-682, Article "Absorption."

² Khanikoff & Longuine, *Ann. Ch. Ph.* (4), 11, p. 412, 1866.

p	a	p	a	p	a
697.7	1.0289	2002.1	1.1037	2738.3	1.1110
809.0	1.0908	2188.7	1.1023	3109.5	1.1000
1289.4	1.1247	2369.0	1.1182		
1469.9	1.1179	2554.0	1.1055		

While the variations in the value of a are considerable, from their irregularities they seem to be due to experimental error only. In the case of the absorption of sulphur dioxide by water, the variation is somewhat more marked and more regular as is shown by the following table,¹ in which p gives the pressure in meters of mercury, g the weight of gas absorbed and g/p the ratio of the two:

p	.05	.1	.2	.5	1.	1.3
g	.015	.027	.05	.118	.229	.295
g/p	.3	.27	.25	.24	.23	.23

While in the case of the absorption of ammonia by water the table² shows a very marked change.

p	.06	.1	.2	.5	1.	2.
g	.119	.158	.232	.403	.613	.982
g/p	2.	1.6	1.2	.8	.6	.5

It is naturally to be expected that the coefficient of absorption should be dependent upon the temperature; in fact it is a matter of common experience that water can be freed of air by heating, and to a greater extent than would be accounted for by the simple expansion of air. The decrease in the solubility is not propor-

¹ Sims, *Ann. Pharm.*, 118, p. 334, 1861.

² Roscoe & Dittmar, *Ann. Pharm.*, 112, p. 349, 1859.

tional to the change of temperature but can be expressed with fair accuracy by the formula

$$a = A - Bt + Ct^2.$$

The following table gives the value of A , B and C according to Bunsen for water and alcohol, for some of the gases of the previous table, between 0° and 20° C.

WATER.			ALCOHOL.		
A.	B.	C.	A.	B.	C.
SO ₂ 79.8	2.61	.0293	328.	16.8	.8
H ₂ S 4.37	.0837	.000521	17.89	.656	.0066
N ₂ O 1.305	.0454	.000684	4.178	.0698	.00061
CO ₂ 1.7967	.0776	.00164	4.33	.094	.00124
CO .0329	.000816	.0000164	.204		
O ₂ .04115	.00109	.0000226	.284		
N ₂ .0203	.000539	.00001116	.1263	.00042	.000006
H ₂ .0193			.0691	.00015	.000001

Solution of Liquids. — We are familiar with the fact that some liquids will mix in all proportions, some not at all, and others in all proportions up to a certain limit. We may take as examples water and alcohol, which mix in all proportions; water and oil, which do not mix; and water and ether, which when shaken up together and then allowed to come to rest separate into two layers, the upper of ether saturated with water, the lower of water saturated with ether. We may represent the phenomena in the case of substances with limited solubility graphically by a diagram such as that of Fig. 20 where the abscissa represents the temperature of the solution, and the ordinate represents the proportional parts of one of the components,

in per cents for convenience, while the proportional part of the other component is given by the distance measured vertically downward from the horizontal line, the sum of the two being the whole amount of the solution, 100 per cent. For such a mixture as water and ether, which have two proportions of solubility, there will be for a given temperature two points,

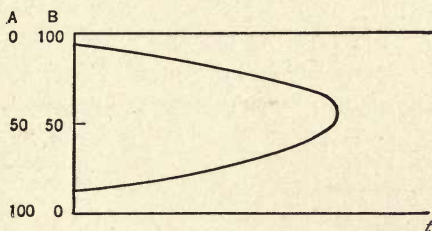


Fig. 20.

or in general, the mutual solubilities of the two liquids at various temperatures will be expressed by two curves, which as the temperature increases gradually approach each other, and for many substances have been found experimentally to meet, as shown in the figure; at or above the temperature represented by this point the two components will dissolve each other in all proportions.

The vapor over the surface of a mixture or solution will in general be a mixture of the vapors of the two components of the solutions, but not necessarily or generally in the same proportions as those which prevail in the solution. Very little work has been done so far in the way of an experimental determination of the composition of such vapors over mixtures. Much

study has been given, however, to the determination of the tension of the vapor over mixtures. The ordinary effect of the addition of a small quantity of a second volatile liquid to a first is to change the tension of the vapor above it not by a large, but by a small amount. The presence of the vapor of the second liquid in addition to that of the first will tend to increase the tension of the resulting vapor, while if the second liquid has quite a marked affinity for the vapor of the first, its vapor will be present in less amount; at any rate, the addition of the small amount of the second liquid in some cases increases the tension of the vapor, in some decreases it, but always by a small amount.

The tension of the vapor over a mixture of liquids can never exceed the sum of the tensions of the vapor of each liquid taken separately at that temperature. This follows immediately from the conceptions of the kinetic theory, by reference to the theory of vaporization. In the process of vaporization, as in the other states of matter, the only forces acting on the molecules are those which we associate with the collisions, and the mutual attractive forces. The attractions between molecules appear, from all our experience of them, to be selective, so that molecules of the same kind appear to exert mutual attractive forces, while molecules of different kinds may or may not seem to attract each other; repulsions do not seem to occur except during the collisions. In a mixture of liquids the two kinds of molecules will in general have some

mutual attraction, otherwise the two liquids would tend to separate. This may be one reason why liquids ordinarily shrink in mixing. A molecule in trying to pass through the non-homogeneous layer will then in general find itself nearer on the average to other attracting molecules, and subject to as great or greater forces tending to return it to the body of the liquid than if the molecules of its own kind only were present. Hence the energy which such molecules must have in order to escape is greater than in the case of the pure liquid, and the number of molecules above the liquid and the partial pressure due to them less than in the case of the vapor over the pure liquid.

This may also be shown as a consequence of thermodynamical considerations. If the tension of the vapor over the mixture be greater than the sum of the tensions of the pure vapors over their pure liquid at the same temperature, then at least one of the vapors must have its partial tension greater than its tension over its pure liquid. If then this vapor be in contact with the mixture and with a body of the pure liquid, at the surface of the latter it will begin to condense, tending to reduce its tension to that giving equilibrium at that surface. This lowering of the tension will result in further evaporation of this component from the mixture, thus giving an automatic process of separation of this component, and since the process of diffusion of a pure substance into a mixture is one which takes place of itself, we have a cycle of processes which

could take place spontaneously and hence be made to do work, at a fixed temperature. That such an isothermal cycle should do useful work is, since the maximum amount of work which can be done in any cycle is proportional to the difference of the extreme temperatures of the cycle, in this case zero, contrary to our general experience as expressed in the Second

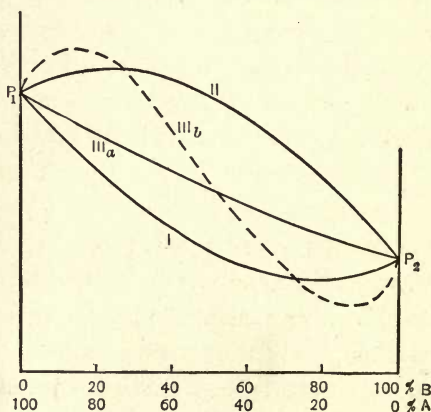


Fig. 21.

Law of Thermodynamics. Hence the assumption that the vapor tension over a mixture of two liquids is greater than the sum of the separate tensions of the component vapors over their pure liquids leads to inadmissible consequences, and is itself inadmissible.

The relation of the vapor tension to the composition of the liquid is readily shown and studied by means of diagrams in which the abscissas represent the proportion of one of the components, that of the other com-

ponent being similarly measured from the other end of the diagram, while the ordinates represent the tension. We then obtain curves of different forms, according as the addition of a small amount of either liquid to the other pure component tends to decrease the vapor tension, (I); or to increase it, (II); or the addition of the second to the first tends to decrease the vapor tension, while the addition of the first to the second increases it, (IIIa and IIIb). Curves¹ like case I are actually observed in the case of mixtures of formic acid and water; case II is that of water and propyl alcohol; and case IIIa that of water and either ethyl or methyl alcohol. Case IIIb has so far never been obtained experimentally, and is only mentioned for the sake of completeness of statement.

In the case of such a mixture as that of water and ether, which separates into two layers, the vapor tension is the same over either layer, the water saturated with ether, or the ether saturated with water; for it is easy to place them in a U-shaped tube so that in one branch one of the solutions, and in the other the other should be exposed to their vapor, while within the tube the two should be in contact. Then according to the considerations adduced a little while ago, there must be a state of equilibrium, with the vapor tension the same over both surfaces, or we should have an automatic isothermal cycle from which we could obtain work, a thing which we believe impossible. The curve of vapor tension over such a solution will then consist

¹ Konowalow, *Wied. Ann.*, 14, p. 34, 1881.

of a straight, horizontal line for all proportions of the mixture between the two stable proportions of saturation, since for any such intermediate proportions the mixture separates into the two parts, and the tension does not depend on the relative amounts of these which are present.

A study of the various shapes of the curves of vapor tension helps to explain the phenomena of distillation, and in particular of fractional distillation. The vapor over a mixture of two liquids will in general be richer than the liquid phase in the more volatile component ; if this vapor be condensed and then redistilled, its resulting vapor will be one of still higher tension, or what amounts to the same thing, if the distillation is at constant pressure rather than at constant temperature, which is the more common case, of lower boiling point than the original liquid. By repeated distillations the liquid is thus separated into two components, one more volatile, the other less volatile. If the curve of vapor tensions be of the form IIIa these two components will be the two pure substances ; if, however, the curve be like that marked I, the residual component will have the composition corresponding to the minimum vapor tension, or least volatility, while the other component will be the pure substance which is present in greater amount in the original mixture than in this residuum ; similarly if the curve be of the form II, the final distillate will be the mixture having highest vapor tension, and the residuum will be the pure substance present in the original mixture in excess.

Osmosis.—It has long been known that certain membranes allow the passage of some substances through them, while they are completely impervious to others; healthy lung tissue allows the oxygen of the air free access to the blood in its capillaries, while completely retaining the blood itself; plants and flowers are freshened by placing them in water, without any appreciable loss of their own soluble constituents. Wishing to obtain further insight into the phenomena of osmosis in plant-cells, that is, the passage of water into and out of them, the botanist, W. Pfeffer,¹ attempted to imitate on a large scale the construction of a plant cell. If we separate a body of a solution and its pure solvent by a portion through which the solvent can pass, but not the dissolved substance, the solvent will diffuse through the partition, thus producing an excess of material, and hence a considerable pressure on the partition. The excess of pressure of the solution over that of the solvent is called *Osmotic Pressure*. In making a satisfactory cell for the study of osmotic phenomena two things are necessary: that it should be completely impervious to the dissolved substance while allowing the solvent to pass through it, and that it should have the mechanical strength to sustain whatever pressure it may need to be subjected to. These conditions seem to be best satisfied by certain films of precipitation, and particularly by a film of copper ferrocyanide. The phenomena of osmosis

¹ "Osmotische Untersuchungen," Leipzig, 1877, Harper's Science Series, IV., p. 3.

can be illustrated qualitatively by placing in a cup of unglazed earthenware, such as is used to separate the liquids in some types of battery cells, a solution of sugar containing a little copper sulphate, closing this cup with a well-fitting cork, carrying a long slim glass tube and well sealed with sealing wax, and immersing the cup completely in a weak solution of potassium ferrocyanide. The copper sulphate and potassium ferrocyanide, meeting in the walls of the cup, will form a film of insoluble copper ferrocyanide which will prevent the passage of the dissolved substances, but not of the water. If then the apparatus be allowed to stand for some time water will gradually enter the cup, causing the solution to rise in the tube, and thus showing that there is an excess of pressure in the inside of the cup. For quantitative work it is necessary to prepare the semi-permeable membrane, as it is called, with much greater care, since the pressures observed may be of considerable magnitude and to replace the open tube of liquid by a form of manometer which shall be able to register a much greater range of pressure, while allowing only a slight increase in the volume of the liquid, and hence only a negligible dilution of the solution. For a more detailed description of methods and immediate results the reader is referred to the original paper.

Osmotic Pressure.—The phenomena of osmosis and osmotic pressure can be observed to best advantage because least complicated by other phenomena in dilute solutions of non-volatile substances. Cane

sugar has been found a convenient material and a few of Pfeffer's results for it are here given.

Osmotic Pressure for Cane Sugar of Different Concentration.

Percentage Conc. By Weight.	Osmotic Pressure.	Pressure/Conc.
1.0	535 mm.	535
2.0	1016 mm.	506
2.74	1518 mm.	554
4.0	2082 mm.	521
6.0	3075 mm.	513

Effect of Temperature on Osmotic Pressure. — The following results were obtained with a 1 per cent. solution of cane sugar :

Temperature.	Pressure.	Comp. Pressure.
14.2° C.	510 mm.	519
32.0° C.	544 mm.	551
6.8° C.	505 mm.	505
13.7° C.	525 mm.	518
22.0° C.	548 mm.	533
15.5° C.	520 mm.	521
36.0° C.	567 mm.	558

It will be seen by a careful inspection of these tables that the osmotic pressure was found to be proportional to the concentration, and to vary uniformly with the temperature. The variations in the third column of the first table, while considerable are not systematic, and the same may be said for the second table of the differences between the second column and the third, which is computed by the formula

$$P = 493(1 + .00367t),$$

Similar results are obtained by direct observations on other substances. Van't Hoff¹ concludes from these facts, first that osmotic pressures follow Boyle's law, which is simply one way of stating that the pressure, whether gaseous or osmotic, is proportional to the concentration. In the formula given above the temperature coefficient is the same as that for ideal gases, and hence he concludes that osmotic pressure follows the law of Gay-Lussac and Charles, and is proportional to the absolute temperature. It has been shown with a considerable degree of exactness that the temperature coefficient of the osmotic pressure is the same for solutions of different substances by the following method: If a protoplasmic cell, animal or vegetable, be placed in a solution whose osmotic pressure is greater than that of the cell, the latter tends to shrink and shrivel; if the osmotic pressure of the solution be less, it tends to swell. This action is sufficiently marked, so that the persistence of the cell in its original state becomes a very sensitive test for the equality of the osmotic pressure within and without the cell. It has been observed that solutions of diverse substances which at any one temperature have the same osmotic pressure as one of these cells, are also at any other temperature in equilibrium with the cell, and hence with each other. The conclusion from these experiments is that the osmotic pressures of different solutions, including the cell-contents, have the same temperature coefficient.

¹*Ztschr. Phys. Chem.*, I., p. 481. Harper's Science Series, IV., p. 13.

To establish completely the relation between the laws of osmotic pressure and of gaseous pressure, it is only necessary to find the relation between the constant factors of proportionality for each substance connecting the pressure at any concentration with the temperature. This may be done either directly or indirectly. By Avogadro's rule and Boyle's law the pressure of an ideal gas is proportional to the number of molecules in unit space. Hydrogen gas, having a density at 0° C. and 760 mm. pressure of .00009 gr. per c.c., or .09 gr. per liter would, if present to the extent of 2 gr. per liter exert a pressure equal to

$$760 \times 2/.09 = 16889 \text{ mm.}$$

If there were such a thing as a "sugar gas," that is, a gas composed of sugar molecules and behaving as an ideal gas, this would exert this same pressure if present to the amount of 342 grams per liter, this being the molecular weight of sugar, and if present to the amount of 10 grams per liter would exert a pressure of

$$16889 \times 10/342 = 493 \text{ mm.}$$

Now 10 grs. per liter is very nearly the amount of sugar present in a 1 per cent. solution, and 493 is exactly the number used in the formula giving the relation of the osmotic pressure to the temperature as the osmotic pressure at 0° C. Hence the evidence of experiment is that the sugar in solution gives an osmotic pressure very nearly, perhaps exactly equal, to that

which would be exerted at the same temperature by the hypothetical "sugar gas" having the same number of molecules in the same space. Experiment shows that this relation can be generalized, and that for a great variety of substances the osmotic pressure follows this law, and that independent of the solvents used.¹ Van't Hoff states the relation thus: "Is-osmotic solutions contain the same number of molecules of the dissolved substance in the same volumes at the same temperature and this number is the same that would be contained in the same volume of an ideal gas at the same temperature and pressure."

Osmotic pressure may also be studied by indirect methods. The osmotic pressure is the pressure which must be exerted to prevent more of the solvent from uniting with the dissolved substance when the solution and the pure solvent are separated by a semi-permeable membrane. But the solvent and dissolved substance may be separated by other means than by forcing the solvent through a membrane, for instance by the process of vaporization, or of crystallization, or by presenting another solvent which will dissolve only one of the components. According to circumstances either the solvent or the dissolved substance may be removed from the solution by either of the three methods. A fairly complete discussion of them all is given by Nernst.² We shall here discuss only the case of the removal of the solvent from the solution. Suppose

¹ W. C. D. Whetham, *Phil. Mag.* (6), 5, p. 282, 1903.

² "Theoretical Chemistry," trans. by Palmer, p. 124.

the solution contained in a receptacle closed at the lower end by a semi-permeable membrane, and continued above in a long narrow tube open at the top. Suppose this receptacle set in a jar of the pure solvent of sufficient depth to keep the semi-permeable membrane covered by the solvent, and further imagine the jar tall enough to enclose the long tube, and hermetically sealed. Then the solution and the solvent

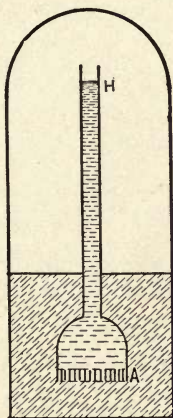


Fig. 22.

are separated in different places by the walls of the receptacle, by the semi-permeable membrane, and by the space above the liquids saturated with the vapor of the solvent. If the dissolved substance is not volatile, all these are completely impermeable to it, while the pure solvent is able to pass from one body of liquid to the other either through the membrane, or through the vapor by the process of vaporization and

condensation. When a state of equilibrium is attained the upper surface of the solution in the long tube will be higher than the surface of the solvent in the jar outside, and the hydrostatic pressure due to the difference of level is then equal to the osmotic pressure. We can state as a general proposition that the vapor tension of the vapor of the pure solvent over the solution must be less than its tension over the solvent, for if it were not, we might have an isothermal cycle in which the vapor of the solvent should be set free at the surface of the solution, then at the surface of the pure solvent, being at a pressure greater than that at the surface of the solution by the hydrostatic pressure of a column of vapor the height of the column of solution, and hence at a pressure greater than the maximum tension over the pure solvent, it would condense, and then pass through the semi-permeable membrane into the solution, a cycle which would take place spontaneously and hence offer the possibility of doing external work. The denial of the existence of such a cycle leads to the declaration that when a state of equilibrium is attained the difference between the vapor pressures on the surfaces of the solution and of the solvent is equal to the hydrostatic pressure of the column of vapor equal in height to the difference between their levels. If we let

h = difference of level of liquids,

S = density of solution,

p_1 = vapor tension over solvent,

p_2 = vapor tension over solution,

M = molecular wt. of solvent,

v = vol. of 1 gr. molecule,

$d = M/v$ = mean density of vapor,

the osmotic pressure will be

$$P = hS,$$

and the difference of vapor tensions will be

$$p_1 - p_2 = hd = \frac{hM}{v}.$$

If we assume that the vapor behaves as an ideal gas the equation

$$pv = RT$$

enables us to eliminate v , giving

$$p_1 - p_2 = \frac{hpM}{RT},$$

and eliminating h

$$(50) \quad P = \frac{p_1 - p_2}{p} \cdot \frac{S}{M} RT,$$

where p is a mean value of the pressure, intermediate between p_1 and p_2 and hence the fractional expression has a value between $(p_1 - p_2)/p_1$ and $(p_1 - p_2)/p_2$. A more rigorous deduction gives its value as $\log p_1/p_2$ and hence

$$(51) \quad P = \frac{S}{M} RT \log \frac{p_1}{p_2}.$$

Osmotic pressure can be determined either directly by observing the depression of the vapor tension and

computing by one of the formulæ just deduced, or by observing the elevation of the boiling point or depression of the freezing point of the solvent occasioned by the addition of the dissolved substance. The theory of these last methods is intimately related to that of the depression of the vapor tension, and their formulæ can be deduced from the last one obtained. In Chap. V. on Change of State we have deduced the formula for the latent heat of vaporization,

$$(29) \quad L = T(v_2 - v_1) \frac{\partial p}{\partial T}.$$

v_1 , the specific volume of the liquid is small in comparison with v_2 , the specific volume of the vapor, and if we neglect the former and assume that the behavior of the latter is represented nearly enough for our purposes by the equation for ideal gases, this becomes

$$L = T \frac{RT}{p} \frac{\partial p}{\partial T},$$

$$\frac{dp}{p} = \frac{L}{RT^2} dT,$$

$$\log p = -\frac{L}{RT} + C,$$

where C is a constant of integration. If T_0 be the boiling point and B the pressure corresponding,

$$\log B = -\frac{L}{RT_0} + C,$$

subtracting

$$\log \frac{p}{B} = \frac{L}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right).$$

If the elevation of the boiling point is small we may call it t and obtain the equation

$$\log \frac{p}{B} = \log \frac{p_1}{p_2} = \frac{L}{R} \frac{t}{T_0^2},$$

and substituting this value

$$P = \frac{SL}{M} \frac{t}{T_0}.$$

Now by comparison of the various equations it appears that L was the amount of energy in mechanical measure required to vaporize one gram molecule of the solvent, and hence L/M is the energy required to vaporize one gram and differs from the ordinary value of the latent heat, λ , only by the factor J . This gives us the form

$$(52) \quad P = SJ\lambda \frac{t}{T_0}.$$

An interesting special form is that for the osmotic pressure of a substance dissolved in water which is

$$P = 57t,$$

where P is expressed in atmospheres.

The freezing point may be defined as the temperature at which the solid, liquid and vapor phases can coexist in equilibrium. For both the processes of vaporization and of sublimation the equation for latent

heat which we wrote a little while ago holds good, hence if L and p refer to vaporization from the liquid and L' and p' to sublimation from the solid,

$$\log p = -\frac{L}{RT} + C,$$

$$\log p' = -\frac{L'}{RT} + C'.$$

If the freezing point be T_0 and the vapor tension corresponding be p_0 , then

$$\log p_0 = -\frac{L}{RT_0} + C,$$

$$\log p_0 = -\frac{L'}{RT_0} + C'.$$

Eliminating C , C' and p_0 by successive subtractions,

$$\log \frac{p}{p'} = \frac{L' - L}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right).$$

Now in this expression p is the vapor tension over the pure solvent at the temperature T , and p' is the tension over the pure ice of the solvent at that temperature, and hence, from the condition of equilibrium, over the solution; hence we may substitute this value of the logarithm in the equation for the osmotic pressure, which becomes

$$P = \frac{S(L' - L)}{M} \frac{t}{T_0},$$

and since $(L' - L)/M$ is the amount of energy required to melt one gram of the solvent, if we represent the ordinary latent heat of fusion by μ this becomes

$$(53) \quad P = S/\mu \frac{t}{T_0}.$$

For water this becomes, in atmospheres,

$$P = 12.07t.$$

It readily appears that the indirect methods of determining the osmotic pressure are not capable of as great accuracy as the direct method might give if we could find a membrane of satisfactory strength and rapidity of action. On account of its simplicity and convenience the freezing point method is oftenest used, and as often only an approximate value of the osmotic pressure is desired in order to check determinations of molecular weight, its accuracy is found sufficient to determine which of two or more otherwise equally allowable values is to be selected.

We have then three equations relating the osmotic pressure to the depression of the vapor tension, the elevation of the boiling point, and the depression of the freezing point, respectively, of the solvent ;

$$(50) \quad P = \frac{p_1 - p_2}{p} \frac{S}{M} RT,$$

$$(52) \quad P = S/\lambda \frac{t}{T_0},$$

$$(53) \quad P = SJ\mu \frac{t}{T_0}.$$

We have also the law experimentally discovered by Raoult¹ that the relative lowering of the vapor tension experienced by a solvent on dissolving a foreign substance is equal to the ratio of the number of dissolved molecules, n , to the number of molecules, N , of the solvent, that is

$$\frac{p_1 - p_2}{p} = \frac{n}{N},$$

$$P = \frac{nS}{NM} RT.$$

But NM is the number of grams of the solvent containing n gram-molecules of the dissolved substance, or NM/n the number containing 1 gram-molecule, and NM/nS the volume of the solvent, which we may call V , hence

$$P = \frac{RT}{V}, \quad PV = RT;$$

hence in a dilute solution, for which Raoult's law holds, and for which the approximations made are allowable, as for instance the assumption that the volumes of the solvent and solution are the same, the osmotic pressure follows the gas-laws. This is an incidental and indirect verification, but still resting upon experimental evidence. Other evidence of about equal weight can be adduced from the discussion of

¹ *Ztschr. Phys. Chem.*, 2, p. 353, 1888.

experiments in which the dissolved substance is removed in one way or another from the solution.

Thermodynamics. — We have so far tacitly assumed that the solutions we are considering are such that if the pure solvent be added to them it will diffuse without any resulting change of temperature, that is, that the heat of dilution is zero. It may be shown experimentally that when this is the case, the osmotic pressure is proportional to the absolute temperature. This may be shown also by the principles of thermodynamics. The equation for the first law of thermodynamics may be written

$$\begin{aligned} dQ &= dU + dW \\ &= \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv + dW. \end{aligned}$$

If now a quantity of the pure solvent and of the solution be allowed to mix freely without doing any work, and without applying heat or cold, we have dQ and dW both vanishing, and hence

$$0 = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv,$$

and if the heat of dilution be zero, there will be no change of temperature, that is, $dT = 0$ and hence

$$\frac{\partial U}{\partial v} dv = 0.$$

But if by v we mean the volume accessible to the dis-

solved substance, and by U the energy of its molecules

$$dv \neq 0,$$

and hence

$$\frac{\partial U}{\partial v} = 0.$$

The second law

$$TdS = dU + dW$$

may also be written

$$T \frac{\partial S}{\partial T} dT + T \frac{\partial S}{\partial v} dv = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv + p dv,$$

which may be separated, since T and v are entirely independent, into the two equations

$$T \frac{\partial S}{\partial T} = \frac{\partial U}{\partial T},$$

$$T \frac{\partial S}{\partial v} = \frac{\partial U}{\partial v} + p;$$

dividing by T

$$\frac{\partial S}{\partial T} = \frac{1}{T} \frac{\partial U}{\partial T},$$

$$\frac{\partial S}{\partial v} = \frac{1}{T} \left(\frac{\partial U}{\partial v} + p \right),$$

differentiating partially by v and T respectively

$$\begin{aligned} \frac{\partial^2 S}{\partial T \partial v} &= \frac{1}{T} \frac{\partial^2 U}{\partial T \partial v} = \frac{1}{T} \left(\frac{\partial^2 U}{\partial v \partial T} + \frac{\partial p}{\partial T} \right) - \frac{1}{T^2} \left(\frac{\partial U}{\partial v} + p \right), \\ \frac{\partial p}{\partial T} &= \frac{1}{T} \left(\frac{\partial U}{\partial v} + p \right). \end{aligned}$$

And if

$$\frac{\partial U}{\partial v} = 0,$$

$$\frac{\partial p}{\partial T_{(v)}} = \frac{p}{T},$$

$$\frac{p}{T_{(v)}} = \text{const.}$$

Or in words, if $\partial U/\partial v = 0$, then when the volume is kept constant, that is, the concentration kept the same, the pressure will be proportional to the absolute temperature; but this condition holds true for the osmotic pressure if the heat of dilution is zero. Conversely we can show by a reversal of our argument that if the osmotic pressure is proportional to the absolute temperature the heat of dilution is zero, and this latter is then the necessary and sufficient condition for the former. In any other case the osmotic pressure must depart from the simple gas laws.

CHAPTER X.

KINETIC THEORY OF SOLUTIONS.

WE shall confine ourselves in the main to the study of solutions in which the dissolved substance is non-volatile, the vapor consequently consisting of molecules of the solvent only. Within the solution we must believe that the molecules both of the dissolved substance and of the solvent are moving freely, and that as they are at the same temperature they have the same mean kinetic energy of translation. It seems equally certain that in solutions as in pure liquids the cohesive or intermolecular forces are of large amount. The phenomenon which we have to accept as fundamental is that certain films allow the passage of molecules of one sort and not of the other. Two classes of these films are observed, the solid semi-permeable films, which may be animal or vegetable membranes, or membranes of precipitation, and the free surface of the liquid. The behavior of the first class of membranes is comparatively simple, and whatever may be the mechanism by which it allows one kind of molecule to pass through it, while stopping other kinds, the fact itself is sufficient to account in general for the phenomena observed.

The free surface of the solution allows the molecules of the solvent to pass from the liquid to the

vapor regions and back in the same general manner which we have described in Chapter VII. on Vaporization; the passage of the molecules of the dissolved substance through this surface is entirely prevented. What may be the cause of this, how it is that the molecular forces are able to prevent any of these molecules from penetrating through this surface we do not know. For present purposes however we may rest satisfied with the fact: these forces probably act through a region whose thickness is considerable as compared with the dimensions of molecules, so that there is in this region a gradual diminution in the number of molecules of the dissolved substance as one passes toward the free surface. We can then consider that in the main body of the solution the molecules of the dissolved substance are uniformly distributed, but that just at the surface there is a film into which they never penetrate, which is consequently composed only of molecules of the solvent, this film constituting a sort of buffer between the solution and the vapor over it, and being, if you choose, the semi-permeable membrane.

The generalized form of van der Waals' equation we have written

$$(45) \quad (p + P)(v - b) = RT.$$

If we use the subscripts α and β to refer to the vapor and liquid states respectively, and call the covolume $v - b$, Φ , this becomes for the solution, in which the external vapor pressure is negligibly small as compared with the molecular pressure

$$(46) \quad P_b \Phi_b = RT.$$

This equation holds equally well, with the change of subscripts, either of the pure solvent or of the solution, the value of R being the same for quantities of the liquid containing the same number of molecules, since for the same temperature the mean kinetic energies of the different kinds of molecules are the same, and

$$RT = \frac{1}{3} \Sigma mc^2.$$

If we let the subscript b refer to the solution and w to the solvent, which for convenience we shall speak of as water, then for equimolecular quantities of the two liquids

$$P_w \Phi_w = P_b \Phi_b = RT.$$

The pressure P_b within the solution may be thought of as made up of two partial pressures, P_{bw} due to the water molecules, and P_{bs} due to the molecules of the dissolved substance. To determine the ratios of these exactly would require a careful study of the mean free paths of two kinds of molecules in a mixture where the distances between the molecules are of the order of the dimensions of the molecules; on account of the exceeding difficulty of this determination we shall content ourselves, as a first approximation, with the assumption that these partial pressures are proportional to the numbers of molecules which occasion them. We shall call these numbers W and S respectively, and the whole number of molecules N . Then

$$W + S = N$$

and the partial pressures are

$$P_{bw} = \frac{W}{N} P_b,$$

$$P_{bs} = \frac{S}{N} P_b,$$

$$P_{bw} + P_{bs} = P_b.$$

In Chapter VII. we deduced the relation between the latent heat of vaporization of the pure solvent and its pressures

$$(48) \quad L_w = RT \log \frac{p_w + P_w}{p_w + P_a} + (P_w - P_a) b_w,$$

which, neglecting in each case the smaller pressure, becomes

$$L_w = RT \log \frac{P_w}{p_w} + P_w b_w.$$

Following the reasoning of the same chapter, if N be the number of molecules in one gram molecule, and Φ_b the covolume of one gram molecule in the solution, then the number of molecules per unit covolume will be N/Φ_b and the number of these striking a given unit of area in one second will be¹

¹ Strictly, the number is the sum of the two expressions

$$\frac{W}{\Phi_b} \frac{\beta_w}{2\sqrt{\pi}} + \frac{S}{\Phi_b} \frac{\beta_s}{2\sqrt{\pi}}$$

but as only the first term is used, no error is introduced by this inaccuracy of form.

$$\frac{N}{\Phi_b} \frac{\beta}{2\sqrt{\pi}}.$$

But if we consider the unit area as taken between the homogeneous solution and the thin surface film of solvent which the dissolved molecules cannot penetrate, the number passing this unit of area is the number of molecules of the solvent which reach it, namely,

$$\frac{W}{\Phi_b} \frac{\beta}{2\sqrt{\pi}}$$

This then is the number of molecules of solvent passing up from the solution into the surface film of pure solvent per unit area in one second. This surface film is also the non-homogeneous layer through which the vaporization takes place. But considering a thin portion of it, next to the solution, so thin that in it the covolume can be considered as a constant, if we call this covolume ϕ , then the number of molecules passing down from this portion into the solution through unit area in one second will, by the same reasoning, be

$$\frac{N}{\phi} \frac{\beta}{2\sqrt{\pi}}.$$

Since these numbers must be the same, for equilibrium,

$$\frac{W}{\Phi_b} = \frac{N}{\phi},$$

$$\phi = \frac{N}{W} \Phi_b.$$

That is, the solution is covered by a surface film of pure solvent, whose lower portions, in contact with the solution, have a covolume greater than that of the solution in the proportion of N to W . Then the expression for the latent heat of vaporization as the work of the molecules in passing through this non-homogeneous layer, which we had written

$$(47) \quad L = RT \int \frac{v dv}{(v - b)^2}$$

becomes, introducing ϕ as the variable of integration, and considering that the molecule has to pass from the lowest part of the surface film of solvent into the vapor

$$L_b = RT \int_{\phi = N\Phi_b/W}^{\phi = v_a - b_w} (\phi + b_w) \frac{d\phi}{\phi^2}.$$

which gives us, if we assume that b_w is a constant,

$$L_b = RT \left[\log \frac{v_a - b_w}{N\Phi_b/W} - \frac{b_w}{v_a - b_w} + \frac{b_w}{N\Phi_b/W} \right],$$

which by comparison with the equations

$$P_b \Phi_b = RT, \quad P_{bw} = \frac{W}{N} P_b,$$

and disregarding small quantities as before, reduces to the form

$$L_b = RT \log \frac{P_{bw}}{P_b} + P_{bw} b_w,$$

which is entirely analogous to the expression written for a pure solvent, substituting for the molecular pressure of the pure solvent its partial pressure in the

solution. Subtracting this equation from the other, and replacing $L_w - L_b$ by L_s , the heat of dilution,

$$L_s + RT \log \frac{p_w}{p_b} = RT \log \frac{P_w}{P_{bw}} + (P_w - P_{bw})v_w.$$

This expression is perfectly general; in the case of dilute solutions, where P_w and P_{bw} are very nearly the same we may write

$$RT \log \frac{P_w}{P_{bw}} = RT \frac{P_w - P_{bw}}{P_w} = \Phi_w(P_w - P_{bw}),$$

and

$$L_s + RT \log \frac{p_w}{p_b} = (P_w - P_{bw})v_w.$$

In the case where the heat of dilution is zero, this may be written

$$P_w - P_{bw} = \frac{RT}{v_w} \log \frac{p_w}{p_b}.$$

Comparing this with the equation deduced in the last chapter,

$$(51) \quad P = \frac{S}{M} RT \log \frac{p_1}{p_2},$$

we see that $p_w = p_1$ is the vapor tension over the pure solvent, $p_b = p_2$ is the tension over the solution and v_w is the volume occupied by a gram molecule of this solvent, M/S , and hence

$$P = P_w - P_{bw},$$

that is, the osmotic pressure here appears as the difference between two molecular pressures. More explicitly, if a solution and a quantity of its pure solvent, both under the same external pressure, be placed in

communication with each other through a semi-permeable membrane, the molecular pressure in the pure solvent will be greater than the partial molecular pressure of the solvent in the solution, and hence the molecules of the solvent will tend to pass into the solution, and to prevent this passage it is necessary to apply a hydrostatic pressure to the solution equal in amount to the difference between these molecular pressures. This hydrostatic pressure is what is measured in the direct determinations of osmotic pressures.

The expression $P_w - P_{bw}$, which we have just found to be the osmotic pressure, can be reduced to a slightly different form,

$$P_w - P_{bw} = P_w - \frac{W}{N} P_b = P_w - \frac{N - S}{N} P_b,$$

which reduces, if $P_b = P_w$ to the form

$$\frac{S}{N} P_w.$$

That is, the osmotic pressure is proportional to the concentration or to the number of molecules of the dissolved substance, if the molecular pressure is the same both for the pure solvent and for the solution; in this case also the covolume will be the same. That this last condition should hold rigidly is hardly to be expected, yet that it does hold approximately is shown by the experimental discovery of Raoult's law, which states the same relation of proportionality to the number of molecules.

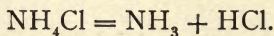
CHAPTER XI.

DISSOCIATION AND CONDENSATION.

WHEN the atoms or radicals which go to make up the molecules of an aggregate are capable of uniting in different combinations, which shall result in different kinds of molecules, and are also capable of being rearranged by suitable interchanges, so that the molecules of certain sorts shall be made to increase in number at the expense of molecules of other sorts, our experience as formulated in the teachings of physical chemistry shows that such interchanges may take place of themselves, without the intervention of external controls. A familiar example, which may serve to give definiteness to our ideas is the reaction often known as double decomposition, such as the reaction of sulphuric acid and common salt to form hydrochloric acid and sodium sulphate, in accordance with the formula



Still simpler are the reactions classed together under the name of *dissociation*, of which a striking case is the dissociation of ammonium chloride on vaporization, in accordance with the formula



From the standpoint of chemical dynamics these reac-

tions are reversible, that is, may take place in either direction, and in any actual case will probably take place in both directions, with speeds depending upon the temperature and pressure of the aggregate and upon the concentration of the various kinds of molecules. According to these views equilibrium is attained simply when the reactions in the two directions are of such speed as to leave the composition of the aggregate unchanged.

Kinetic Theory of Dissociation.—Dissociation of a gas which results in a change of the number of molecules reveals its presence by anomalous vapor pressure, or vapor density, according to the circumstances of the experiment. When the dissociation is complete, we have only the problem, already solved at least approximately, of a mixture of two gases. But in many cases the dissociation is only partial, and is found to depend either upon the temperature or upon the density of the gas.

One possible explanation is that given by Boltzmann¹ and in slightly different forms by others. According to this view, whenever two atoms or radicals which are capable of uniting with each other come sufficiently near to each other, and in suitable relative position, they are to be considered as forming one complex molecule. The problem is to find the relative number of such pairs of atoms, among all the atoms present, which are in general so situated relatively as to be considered as chemically combined, under the exist-

¹ "Gasttheorie," II., pp. 177-217.

ing conditions of mutual attraction, temperature, pressure and volume. This treatment gives the degree of dissociation as a function of the temperature and pressure.

Another explanation, different in form, but not necessarily contradicting the first, is this : the kinetic energy of any molecule consists of that associated with its motion of translation, and that associated with the relative motions of its parts. This latter motion has a tendency to separate the parts of the molecule, so that any collision between two molecules which is so conditioned as to increase the energy of the internal motions of one of these molecules beyond a certain amount will result in its actual disruption. Of course we do not know that there is any simple relation between the amount of internal energy of an individual molecule and its external energy. But we have come to believe that for any large body of gas the total internal energy has a definite ratio to the total energy of translation of the molecules (p. 73) this ratio being independent of the pressure and density, and probably also of the temperature of the gas. We have no evidence that the molecules attaining the highest internal energy are identically those that attain the highest speeds, but it is reasonable and necessary to believe that the distribution of energies follows the same laws. In the same way, while we are not able to say anything as to the results of any single collision of two molecules, since the relative numbers of molecules having the different speeds is constant, in any large number of collisions, the resulting speeds of

the individual molecules must have the same distribution, and the resulting internal energies must have a distribution entirely similar to that of the external energies of translation.

We can make these conceptions more definite by applying them to the simplest case of dissociation, that in which the molecule is dissociated into two like parts, as in the case of iodine vapor, $I_2 = 2I$ or nitric oxide, $N_2O_4 = 2NO_2$. If the whole number of molecules, when undissociated, be N , we shall consider that part of these, N_1 molecules, remain undissociated, while the remainder, N_2 molecules, dissociate forming $2N_2$ of the simpler molecules, so that the resulting gas contains $N_1 + 2N_2$ molecules, while the original gas contained $N_1 + N_2 = N$ molecules.

Suppose that the critical internal energy just capable of producing dissociation corresponds to the speed c_1 then the number of collisions in any given time resulting in such dissociation will be proportional to the number of collisions of the undissociated molecules, $N_1 P_1 = N_1 \bar{c}/l_1$ (p. 60) and to the probability of speeds above the critical speed c_1 ,

$$\int_{c_1}^{\infty} \frac{4}{\alpha^3 \sqrt{\pi}} e^{-c^2/\alpha^2} c^2 dc$$

(p. 25) that is, to the product

$$\frac{4N_1 \bar{c}}{\sqrt{\pi} l_1 \alpha^3} \int_{c_1}^{\infty} e^{-c^2/\alpha^2} c^2 dc.$$

Writing x for c/α , and applying formulæ of integra-

tion developed on pp. 27 and 31,

$$\begin{aligned} \frac{4N_1\bar{c}}{\sqrt{\pi}l_1} \int_{x_1}^{\infty} e^{-x^2} x^2 dx &= \frac{4N_1\bar{c}}{l_1} \left[-\frac{1}{2} x e^{-x^2} + \frac{1}{2} \int e^{-x^2} dx \right]_{x_1}^{\infty} \\ &= \frac{2N_1\bar{c}e^{-x_1^2}}{\sqrt{\pi}l_1} \left[x_1 + \frac{1}{2x_1} - \frac{1}{4x_1^3} + \dots \right], \end{aligned}$$

in which all the terms of the series except the first two may ordinarily be neglected, since c_1 is to be regarded as very large in comparison with α , and hence $x_1 = c_1/\alpha$ is very large.¹

Since the dissociated and undissociated parts of the gas, being thoroughly mixed, are at the same temperature, and hence have the same average kinetic energy per individual particle, and since the former have only half the mass of the latter, their speed will be greater in the ratio $\sqrt{2} : 1$ so that the number of collisions of one of these dissociated molecules taking place with its speed less than a certain critical speed c_2 would be

$$P_2 \int_0^{c_2} \frac{4}{(\sqrt{2}\alpha)^3 \sqrt{\pi}} e^{-c^2/2\alpha^2} c^2 dc,$$

where P_2 , the number of collisions per second of a dissociated particle, can be replaced by $\sqrt{2}\bar{c}/l_2$ and we may write $x = c/\sqrt{2}\alpha$, giving

¹ Jaeger, in Winkelmann's "Handbuch," II., 2, pp. 563-4, assumes that c can be substituted for \bar{c} , while in this integration $c > c_1 > \bar{c}$ so that the result here found ought to be more accurate.

$$\frac{4\sqrt{2c}}{\sqrt{\pi}l_2} \int_0^{x_2} e^{-x^2} x^2 dx.$$

The probability that the other party to the collision shall have a similarly low speed is, using y instead of x ,

$$\frac{4}{\sqrt{\pi}} \int_0^{y_2} e^{-y^2} y^2 dy,$$

so that the number of collisions between pairs of such molecules is represented by the product of these two quantities by $2N_2$, the number of such particles, and divided by 2, since each collision involves two of them, giving

$$\frac{16\sqrt{2}N_2c}{\pi l_2} \int_0^{x_2} e^{-x^2} x^2 dx \int_0^{y_2} e^{-y^2} y^2 dy.$$

Since the speeds of different molecules are entirely independent, we may multiply these expressions under the radical sign, giving

$$\frac{16\sqrt{2}N_2c}{\pi l_2} \int_0^{x_2} \int_0^{y_2} e^{-x^2-y^2} x^2 y^2 dx dy$$

and remembering that the only requisite is that the total energy of the two particles shall not exceed a given limit, that is that $x^2 + y^2$ shall not exceed a given value, say r^2 , we can let $x = r \cos \theta$, $y = r \sin \theta$ and integrate between proper limits, giving

$$\frac{16\sqrt{2}N_2c}{\pi l_2} \int_0^r \int_0^{\pi/2} e^{-r^2} r^2 \cos^2 \theta r^2 \sin^2 \theta r dr d\theta.$$

The expression to be integrated becomes, on separating the variables

$$\int_0^r e^{-r^2} r^5 dr \int_0^{\pi/2} \cos^2 \theta \sin^2 \theta d\theta = \frac{\pi}{16} \int_0^r e^{-r^2} r^5 dr,$$

which can be integrated by successive applications of formula (8) on p. 27, giving

$$\frac{\pi}{16} \left[1 - \frac{e^{-r^2}}{2} (r^4 + 2r^2 + 2) \right],$$

so that our original expression becomes, writing x_2 for r ,

$$\frac{\sqrt{2N_2c}}{l_2} \left[1 - \frac{1}{2} e^{-x_2^2} (x_2^4 + 2x_2^2 + 2) \right].$$

In reviewing the development of these expressions we need to remember that the speeds c and the ratios x are used merely as a means of determining the numbers of collisions having certain properties, while the real point at issue is whether the *internal* energy of a given molecule exceeds (or falls below) a certain limit. The difference in treatment of the two cases arises from the fact that in the first case we consider the result to one molecule only, while in the second we are interested in a result involving two, namely that the two colliding particles shall have the sum of their energies less than a certain amount, and that they shall actually combine and remain together for a time.

Whenever a steady state of dissociation is attained, not only will the temperature of the dissociated and undissociated portions be the same, but the number of molecules dissociating and the number of collisions resulting in reassociation of molecules will be the same, that is,

$$\frac{2N_1\bar{c}e^{-x_1^2}}{\sqrt{\pi}l_1}\left(x_1 + \frac{1}{2x_1}\right) \\ = \frac{\sqrt{2}N_2\bar{c}}{l_2}\left[1 - \frac{1}{2}e^{-x_2^2}(x_2^4 + 2x_2^2 + 2)\right],$$

in which \bar{c} has the same meaning on both sides, l_1 and l_2 depend upon the dimensions of the different kinds of molecules, and x_1 and x_2 are ratios depending upon the temperature of the gas, and upon the requisite energies at which the dissociation and reassociation take place, or in other words, the temperatures of dissociation and condensation.

We have not yet taken account of the effect of varying density upon the degree of dissociation. Experiment indicates that dissociation is less as the density is greater, or in other words, is greater as the volume, and the mean free path, increase. This may be due to the greater number of triple or multiple collisions, or of collisions following so closely as to be regarded as multiple in the more dense gas. We may take account of this by multiplying the first member of the equation just deduced by al_1 in which a is simply a factor of proportionality. Doing this, and introducing another value of l_2 , namely

$$l_2 = \frac{1}{\sqrt{2\pi n\sigma^2}},$$

in which

$$n = \frac{2N_2}{v},$$

and dividing by $2\bar{c}$

$$\frac{aN_1 e^{-x_1^2}}{\sqrt{\pi}} \left(x_1 + \frac{1}{2x_1} \right) = \frac{2\pi N_2^2 \sigma^2}{v} \left[1 - \frac{1}{2} e^{-x_2^2} (x_2^4 + 2x_2^2 + 2) \right],$$

$$N_1 = \frac{N_2^2}{v} \frac{2\pi \sigma^2 \left[1 - \frac{1}{2} e^{-x_2^2} (x_2^4 + 2x_2^2 + 2) \right]}{a e^{-x_1^2} \left(x_1 + \frac{1}{2x_1} \right)}$$

which may also be written

$$N_1 = \frac{N_2^2}{v} f(t).$$

If the gas be sufficiently rarefied to follow the laws of ideal gases, aside from the dissociation, its behavior can be represented by the equation

$$pv = k(N_1 + 2N_2)(1 + \alpha t),$$

where k is a suitable constant, and α the coefficient of expansion. Multiplying together the appropriate members of the last two equations, and dividing by

$$k(1 + \alpha t)N_2^2,$$

$$p \frac{f(t)}{k(1 + \alpha t)} = \frac{N_1^2}{N_2^2} + 2 \frac{N_1}{N_2} = z,$$

$$\frac{N_1}{N_2} + 1 = \sqrt{1 + z},$$

$$\frac{N_1}{N_2} = \sqrt{1 + z} - 1, \quad \frac{N_1 + N_2}{N_2} = \frac{N}{N_2} = \sqrt{1 + z};$$

or in other words, the proportion of the original

molecules which are dissociated is

$$\frac{N_2}{N} = \frac{1}{\sqrt{1+z}},$$

where z is defined as a function of p and t by two preceding equations.

From this last result,

$$N_2 = \frac{N}{\sqrt{1+z}},$$

$$N_1 + 2N_2 = N + N_2 = N \left(1 + \frac{1}{\sqrt{1+z}} \right),$$

and the law of the gas is

$$pv = kN \left(1 + \frac{1}{\sqrt{1+z}} \right) (1 + \alpha t),$$

differing from that of the ideal gas only in the factor involving z . If the density of an ideal gas at a given pressure and temperature be called d_0 , that of a dissociated gas at the same temperature and pressure d , these densities will be inversely as the volumes, and hence

$$d = \frac{d_0}{1 + \frac{1}{\sqrt{1+z}}}.$$

For numerical computations it is necessary to evaluate x_1 and x_2 as functions of the temperature. In the first case, that of double molecules, the definition was

$$x_1 = \frac{c_1}{\alpha}, \quad x_1^2 = \frac{c_1^2}{\alpha_1^2} = \frac{c_0^2(1 + \alpha t_1)}{\alpha_0^2(1 + \alpha t)},$$

where the first α is the most probable speed of the molecule, and the subscript 0 refers to values at the temperature 0°C . If c_0^2 be regarded as the "mean square," then

$$\frac{c_0^2}{\alpha^2} = \frac{3}{2}, \quad x_1^2 = \frac{3(1 + \alpha t_1)}{2(1 + \alpha t)}.$$

In the second case,

$$x = \frac{c}{\sqrt{2}\alpha}, \quad x^2 = \frac{c^2}{2\alpha^2},$$

and the value of x^2 for each of two particles having the same speed, and having the maximum value of the sum of their energies compatible with reassociation would be

$$\frac{1}{2}x_2^2 = \frac{c_2^2}{4\alpha^2} = \frac{c_{20}^2(1 + \alpha t_2)}{4\alpha_0^2(1 + \alpha t)},$$

where

$$\frac{c_{20}^2}{2\alpha_0^2} = \frac{3}{2},$$

and hence

$$x_2^2 = \frac{3(1 + \alpha t_2)}{2(1 + \alpha t)},$$

which enable us to express $f(t)$ and hence z as functions of t , t_1 , and t_2 .

The assumption that x_2 is very small while x_1 is very large leads to the following simplifications; in the numerator of $f(t)$ we can expand the exponential into a series

$$e^{-x_2^2} = 1 - x_2^2 + x_2^4/2 - x_2^6/3 + \dots,$$

hence, keeping only the first term of the result,

$$1 - \frac{1}{2}e^{-x_2^2}(x_2^4 + 2x_2^2 + 2)$$

$$= 1 - \frac{1}{2}(1 - x_2^2 + \frac{1}{2}x_2^4 - \frac{1}{3}x_2^6)(2 + 2x_2^2 + x_2^4) = \frac{1}{3}x_2^6$$

and similarly rejecting $1/2x_1$ in comparison with x_1

$$f(t) = \frac{2\pi^{\frac{3}{2}}\sigma^2 \cdot \frac{1}{3}x_2^6}{ae^{-x_1^2}x_1}$$

$$= \frac{2\pi^{\frac{3}{2}}\sigma^2}{3a} \cdot e^{\frac{3(1+at_1)}{2(1+at)}} \cdot \frac{27}{8} \frac{(1+at_2)^3}{(1+at)^3} / \sqrt{\frac{3(1+at_1)}{2(1+at)}}$$

$$= B \frac{e^{\frac{\beta}{1+at}}}{(1+at)^{\frac{5}{2}}},$$

where B and β are new constants, and

$$z = p \frac{f(t)}{k(1+at)} = \frac{pB}{k} \frac{e^{\frac{\beta}{1+at}}}{(1+at)^{\frac{5}{2}}}$$

$$= A \frac{e^{\frac{\beta}{1+at}}}{(1+at)^{\frac{5}{2}}},$$

a result which differs only very slightly from

$$z = A \frac{e^{\frac{\beta}{1+at}}}{(1+at)^3},$$

obtained by Jaeger, on slightly different assumptions. He gives the following tabulation of the density of nitric oxide,¹ in which the computed values are found by

¹ Winkelmann, "Handbuch der Physik," II., 2, p. 568. The table is based upon data given in A. Naumann, "Thermochemie," p. 177.

substituting the values $d_0 = 3.18$, $A = 1501 \times 10^{-11}$, $\beta = 23.83$, in the last equation,

t	d (obs.)	d (comp.)	t	d (obs.)	d (comp.)
26.7°	2.65	2.70	80.6°	1.80	1.79
35.4°	2.53	2.55	90.0°	1.72	1.72
39.8°	2.46	2.46	100.1°	1.68	1.67
49.6°	2.27	2.27	111.3°	1.65	1.64
60.2°	2.08	2.07	121.5°	1.62	1.62
70.0°	1.92	1.92	135.0°	1.60	1.60

The value of β here employed enables us to give an approximate value to t_1 , the dissociation temperature,

$$\beta = \frac{2}{3} (1 + \alpha t_1) = 23.83,$$

$$1 + \alpha t_1 = \frac{2}{3} \cdot 23.83,$$

$$t_1 = 4064^\circ.$$

There is reason for believing that changes in the degree of association, that is, polymerization and dissociation, occur very largely in the liquid and solid states, and in connection with the change from one state to another. Two results follow immediately; the introduction of further corrections into our equation of condition, and a decided increase in the apparent values of the specific heat and the latent heat of change of state. It is interesting to note that beginning with the type equation

$$p = \frac{Nmc^2}{3(v - b)},$$

and introducing the correction factor due to the dissociation, by simple approximations, based on the assump-

tion that v is large compared with b , either van der Waal's equation or that of Clausius may be deduced.¹

In this connection Sutherland in his paper on "The Molecular Constitution of Water"² has brought forward the view that while steam has its molecule correctly represented by the ordinary formula H_2O , ice is really $(\text{H}_2\text{O})_3$, and water a solution of $(\text{H}_2\text{O})_3$ in $(\text{H}_2\text{O})_2$; on this basis he has developed formulæ which account quantitatively for the behavior of water, often anomalous, in nearly every particular. The triple formula for ice suggests an equilateral triangle as the dominant feature of the form of the complex molecule, which is consistent with the persistence of the angle 60° in its crystals. He finds that the assumption of a density of .88 for liquid $(\text{H}_2\text{O})_3$ (*trihydrol*) and 1.089 for $(\text{H}_2\text{O})_2$ (*dihydrol*) at 0°C. , and proportions varying from 37.5 per cent. by weight of trihydrol at 0° to 21.7 per cent. at 100° , and probably nearly pure dihydrol at the critical temperature, will account for the maximum density at 4°C. , for the diminution of the optical coefficient $(n^2 - 1)/(n^2 + 2)\rho$ with rising temperature, for the peculiarities of the compressibility of water, and for its characteristic surface tension and viscosity. In general, either a rise of temperature, or an increase of pressure, has a tendency to dissociate trihydrol into dihydrol, so that the surface film, in which there is a tension, rather than a pressure, is almost pure trihydrol at tempera-

¹ Winkelmann, "Handbuch der Physik," II., 2, p. 569.

² *Phil. Mag.* (5), 50, pp. 460-489, 1900. Nernst ("Theoretical Chemistry," p. 650) states that work on surface tension indicates a degree of association for water varying from 2.3 to 3.8,

tures below 40° , and is richer in this ingredient at higher temperatures than is the body of the liquid. The large values of the latent heats of fusion and vaporization are easily accounted for by the superposition of latent heats of dissociation; in particular, in the case of fusion, the shrinkage might otherwise even seem to call for a "latent cold" of fusion. For numerical results, reference is made to the original paper.

Electrolytic Dissociation.—Van't Hoff, in an early paper on Osmotic Pressure,¹ noted that while most substances in dilute solution exhibit osmotic pressures very nearly agreeing with those deduced from the gas-laws, there are exceptions which systematically show pressures considerably greater than these, so that to include all cases the equation must be written

$$pv = iRt,$$

where i may have values greater than 1. The limiting value, 1, applies to the non-exceptional cases. Soon afterwards Svante Arrhenius,² a Swedish chemist, suggested a possible method of explaining these exceptions. In the case of gases anomalous densities or pressures are commonly explained on the basis of dissociation. Arrhenius suggested that it was only natural to explain these anomalous osmotic pressures in the same way; Van't Hoff had noticed that the exceptions included all the salts, all the acids, all the alkalies, that is, all the substances which in solution conduct

¹ *Ztschr. phys. Chem.*, I., 481, Harper's Science Series, IV., p. 13.

² *Ibid.*, I., 631, Harper's Science Series, IV., p. 47.

electrolytically. Arrhenius takes up a suggestion made by Clausius¹ in 1857 that a part of the molecules of a solution which conducts electrolytically are dissociated, and that the conduction is by means of these dissociated or active molecules. But he goes further than Clausius by making this idea quantitative, and not merely qualitative. The conductivity of a solution will be proportional to the number of these "active" molecules or ions, and hence from measurements of the conductivity one can determine the "coefficient of activity," α . The method of the determination can be taken up later. Now this coefficient α is intimately related with the coefficient i of Van't Hoff's equation. If a solution contain molecules n in number before their dissociation, and the coefficient of activity be α , then $n\alpha$ will be the number of the original molecules which have suffered dissociation, and $n(1 - \alpha)$ the number remaining undissociated; if each molecule on dissociation forms k parts, then after the dissociation instead of n molecules there will be

$$n(1 - \alpha) + n\alpha k = n[1 + \alpha(k - 1)],$$

and the osmotic pressure will be increased in the same ratio, hence

$$i = 1 + \alpha(k - 1).$$

A first immediate consequence of this theory is that when the electrolyte is largely dissociated, any properties of the solution which are due immediately to the ions themselves should be additive. This may be

¹ *Pogg. Ann.*, 101, p. 347.

tested in general by comparing the property in question for the salts of a given ion with the corresponding salts of some other ion. Thus we are familiar with the characteristic blue of dilute solutions of cupric solutions, the orange of bichromates, the deep purple of permanganates; Ostwald¹ for thirteen salts of permanganic acid has measured the position in the spectrum of four principal absorption bands, and found them identical; so that a colored ion gives its color to the solution regardless of the presence of another ion, and if this second ion be colorless, the effect of the colored one is immediately evident. In fact the use of indicators to determine the acidity or alkalinity of solutions seems to depend upon a difference in color between an undissociated molecule and one of its ions.

Valson² showed that the specific gravity of salt solutions was an additive property, that is, the difference between the specific gravities of equimolecular (dilute) solutions of salts of two given different metals with the same acid was constant, independent of the acid and similarly for the salts of two given acids with the same base. These conclusions have been corroborated by the later work of Ostwald on the change of volume occurring in the case of the neutralization of acids with bases.

Similarly, the molecular refractive constant (either in

the form $\frac{M(n-1)}{d}$ or $\frac{M(n^2-1)}{d(n^2+2)}$ in which M is the

¹ *Ztschr. phys. Chem.*, 9, 584.

² *C. R.*, 73, p. 441, 1874, etc.

molecular weight, and d the density) and the optical activity, that is the power of rotating the plane of polarized light, are additive properties of the ions.

Even more convincing are the results of the study of electrical conductivity, of mixed solutions, and of the heat of neutralization of strong acids and bases. It is a common-place that mixing equimolecular weights of two salts of strong acids and strong bases, as sodium chloride, and potassium bromide, at considerable dilution, the properties of the mixture are indistinguishable from those of a similar mixture of sodium bromide and potassium chloride. This is an obvious necessity, if both salts in each case are completely dissociated, for the two solutions then contain identical mixtures of the four ions, sodium, potassium, bromine, chlorine. But a mixture of methyl chloride and ethyl bromide is entirely distinct in its properties from one of ethyl chloride and methyl bromide, none of these compounds being dissociated in solution.

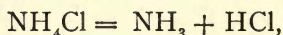
It will appear later that water itself is practically undissociated, hence if a completely dissociated acid solution be added to a completed dissociated alkaline solution, and the resulting salt be soluble and also completely dissociated, the only chemical action which will take place is the union of the hydrogen and hydroxyl radicals, and the heat developed will be independent of the kind of acid and alkali employed. That this is true in the case of strong acids and bases is shown by the following table taken from Nernst.¹

¹ "Theoretical Chemistry," p. 510.

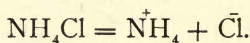
TABLE OF THE HEATS OF NEUTRALIZATION OF ACIDS AND BASES.

Acid and Base.	Heat of Neutralization.
Hydrochloric acid and sodium hydroxide,	13,700
Hydrobromic acid and sodium hydroxide,	13,700
Nitric acid and sodium hydroxide,	13,700
Iodic acid and sodium hydroxide,	13,800
Hydrochloric acid and lithium hydroxide,	13,700
Hydrochloric acid and potassium hydroxide,	13,700
Hydrochloric acid and barium hydroxide,	13,800
Hydrochloric acid and calcium hydroxide,	13,900

The difference between the two types of dissociation is well illustrated by ammonium chloride, which on being vaporized breaks up according to the equation



but in aqueous solution is dissociated into the ions



Electrolytic dissociation then differs in most marked fashion from the gaseous dissociation which we have previously discussed and from the similar dissociation and polymerization in solution, in that the resulting ions carry electric charges, and that these charges are all equal in amount or simple multiples of the unit ionic charge. This latter peculiarity is shown by Faraday's law, that the amount of material going into or out of the solution at either electrode is proportional to the electrical current and the time, that is, to the quantity of electricity involved, and also to the combining weight of the ion; or in other words, the same current sets free chemically equivalent quantities of any

ions in the same time. Ions are univalent, divalent, trivalent, according as they carry once, twice, or three times the unit ionic charge. This definition is in agreement with ordinary chemical usage.

Whenever the ions find themselves in an electrostatic field due to the presence of charged electrodes in the solution, they experience forces tending to make the positive ions move from the positively charged electrode toward the negative, the negative ions in the opposite direction. The resulting drift of charged ions is then the mechanism of the electrolytic conduction of the electric current. It is customary to call the positively charged electrode the anode, the other the cathode, while the positively charged ion, from its tendency to be liberated at the cathode, is called the cation, the negative the anion. Cations include in general metallic and basic atoms and radicals, and the replaceable hydrogen of acids, while anions include acid radicals and hydroxyl.

Anions and cations do not necessarily travel with the same speed. In the extreme case, if one set did not move at all, the current would consist entirely of the carriage of charges of one sign by the ions of that kind, but in the ordinary case, positive charges are being carried away from the anode toward the cathode, and negative charges in the opposite direction, the whole current being thus made up of the sum of these two effects.

If the ions, on arriving at the electrodes, go out of the solution, there is evidently an impoverishment of

the solution at those points, for at an electrode the ions which arrive correspond to a part, only, of the current; while those going out of the solution at that point correspond to the whole current; while if the electrode is dissolved by a secondary reaction regenerating the solution, there is a corresponding concentration of the solution in that region, the new ions, and the newly arrived ions, more than making up for those which have migrated toward the other electrode. In either case, by suitably dividing the solution after the current has passed for some time, and determining by chemical analysis the impoverishment or concentration of the solution in the neighborhood of the electrodes it is possible to determine the ratio of the speeds of migration of the two ions.

Since the passage of the current is a matter of the carriage of charges of both kinds by the ions, the conductivity of a solution is, other things being equal, proportional to the sum of the speeds of migration of the ions. Conductivity data, therefore, together with the data on the ratios of speeds of the molecules, enable us to determine quantities u and v proportional to the ionic speeds, such that

$$\mu = \alpha(u + v),$$

where μ is the molecular conductivity, that is, the actual conductivity divided by the concentration, and α the ionization constant or coefficient of activity. It then appears that the values of u or v for the same ion

in the same solvent are the same, independent of the other ion making up the salt, so that from a table of values of u and v for various ions, the conductivities of solutions of any salts formed from pairs of these ions can be prophesied, if only the degree of dissociation can be foretold. This result is due to Kohlrausch.

It is evidently possible from such data as we have mentioned to deduce the values of the absolute velocities of the ions. According to Kohlrausch the absolute velocities under a potential gradient of one volt per cm. is found by multiplying the relative velocities u and v , by the factor 110×10^{-7} . He gives the absolute velocity of the hydrogen ion, under these conditions as .0032 cm. per second. Lodge¹ filled a long U tube with a solution of gelatine and sodium chloride, colored with phenolphthaleïn with a trace of sodium hydroxide to bring out the red color. This solution hardened sufficiently to prevent any convective mixing but did not seem to affect perceptibly either the true diffusion, or the migration of the ions. The tube was inverted into two vessels containing electrodes immersed in dilute acid. The rate of progress of the hydrogen ions was shown by the retreat of the color in the gelatine tube. The result, corrected for the natural rate of diffusion of the acid, is the rate of advance of the hydrogen ions due to the current. He found, for unit gradient, the values .0029, .0026, .0024. These results, which would naturally be slightly below the true value, correspond satisfactor-

¹ *B. A. Report*, 1886, p. 393.

ily with that computed by Kohlrausch. Wetham¹ has measured the velocity of certain colored ions, observing a level surface between two solutions of different density. His results also confirm the theory. To drive one gram of hydrogen ions through water at the rate of 1 cm. per second, the force required has been computed to be equal to about 320,000 tons weight.

If we imagine a rectangular electrolytic cell² of which two of the parallel surfaces are of platinum 1 cm. apart, the height of the cell being indefinite, introducing a liter of water containing in solution a gram molecule of the salt to be investigated, (*e. g.*, 58.5 g. of common salt) and measuring the resistance between the platinum faces used as electrodes, the reciprocal of this resistance represents the *molecular* conductivity, that is, the conductivity due to the ions produced in that solution from a gram-molecule of salt. If we add more water, making in all two liters, and again determine the conductivity, we shall find it increased. Increasing dilution will still increase the molecular conductivity, but only up to a certain limit, which is reached in the case of this salt at a dilution of about 10,000 liters. The explanation is that the dissociation is at first incomplete, perhaps two thirds of the molecules being dissociated in the normal solution, becoming complete only at great dilutions. The limiting value is often called the molecular conductivity at in-

¹ *Phil. Trans.*, 1893, A, p. 337.

² Walker, "Int. to Phys. Chem.," pp. 220-221.

finite dilution, and indicated by the symbol μ_{∞} . Then the degree of dissociation is represented by

$$\alpha = \frac{\mu}{\mu_{\infty}},$$

while it is evident that

$$\mu_{\infty} = u + v.$$

This latter relation evidently gives a method of obtaining μ_{∞} for compounds for which it cannot be found by direct experiment, if both, or even one of its ions occur in other compounds which can be completely dissociated.

For the compounds which are even at great dilution only partly dissociated, sometimes called half-electrolytes, Ostwald has found that the degree of dissociation is related to the degree of dilution by the equation

$$\frac{\alpha^2}{(1 - \alpha)v} = k,$$

where k is often called the *dissociation constant*. This equation was deduced on theoretical grounds from the law of mass action, a law which was really assumed in the deduction of the law of dissociation of gases, in the earlier part of this chapter. A physical meaning is given to k by making $\alpha = \frac{1}{2}$, when

$$\frac{.5^2}{(1 - .5)v} = k, \quad k = \frac{1}{2v};$$

or in words, k is the reciprocal of twice the volume of dilution necessary to secure the dissociation of one half the molecules of the electrolyte. In the case of acetic acid, for which $k = .000018$, $1/v = .000036$; or a solution of acetic acid .000036th normal would only be one half dissociated.

The strongly dissociated compounds do not follow this law, but other dilution formulæ have been devised, as that of Rudolphi,

$$\frac{\alpha^2}{(1 - \alpha)\sqrt{v}} = \text{Const.},$$

or that of van't Hoff

$$\frac{\alpha^{\frac{3}{2}}}{(1 - \alpha)\sqrt{v}} = \text{Const.},$$

which agree fairly well with observed facts, but are purely empirical.

Conductivity depends not only on the degree of dissociation, which affects the number of ions available, but also upon the size of the ions and the viscosity of the solution, which affect their speed. The lessened viscosity accounts for the increase of conductivity in a conducting solution as the temperature is raised. That this is so is shown both by the fact that such increase of temperature may be shown experimentally to affect the degree of ionization only slightly, and by the effect of adding small quantities of alcohol or glycerine, which are known to increase the viscosity of water very greatly, but not to affect the ionization, with a great resulting increase of the electrolytic resistance.

The degree of dissociation of an electrolyte in solution is affected by the presence of other dissolved substances, and particularly by the addition of a second electrolyte containing one ion in common. In this case the dissociation is made measurably less. Such an effect is shown qualitatively by passing HCl gas into a saturated solution of NaCl. The excess of Cl ions causes the recombination of some of the previously dissociated NaCl, which supersaturates the solution with those molecules, resulting in their precipitation. Noyes¹ has used the change of solubility of the only slightly soluble thallous chloride to determine the degree of dissociation of other chlorides in solution, obtaining results consistent with those obtained by the other methods.

It is noticeable that the so-called strong acids or bases are precisely those which are most strongly dissociated in solution, and that electrolytes as a class enter into chemical reactions promptly and vigorously. In fact, the strength of the strong bases and acids seems to be due primarily to their dissociation, their radicals being thus free from "entangling alliances" and ready to enter into any possible combination in much greater numbers than is possible to the radicals of a less completely dissociated compound. In this connection, it is notable that almost all chemical reactions take place either in aqueous solutions or at least in the presence of traces of moisture; so that thoroughly dried chlorine gas seems to have no effect on

¹ *Ztschr. phys. Chem.*, 9, 603; 12, 162; 13, 412; 16, 125.

fused sodium, and either no or very slight action on most other metals; in dry oxygen dried charcoal will burn, but without flame, forming both carbon monoxide and carbon dioxide, while sulphur, boron and phosphorus do not burn at all; dry acid does not affect litmus; dry hydrochloric acid does not form a precipitate when passed through silver nitrate dissolved in ether or benzol, nor act on dry ammonia. These instances could easily be multiplied, but they serve to call attention to the part played by water and ionization in rapid chemical actions. It is true, however, that many reactions are known, some very rapid, which do not seem to be in any way dependent upon the presence of water, or upon dissociation into electrically charged ions.

Special interest centers in the theory of electrolytic cells used as batteries for the production of electric currents. The thermodynamical theory of reversible cells has been given by Helmholtz. Imagine a small cycle, which may be considered as a Carnot's cycle, in the first part of which the battery is allowed to generate a current, working isothermally at the temperature T until it has delivered a unit quantity of electricity. Then the amount of electrical energy developed will be numerically equal to E , the E.M.F. of the cell, while chemical reactions will have taken place which, but for their electrical utilization, would have produced the quantity of heat q ; hence the amount of heat which must be supplied from without to keep the temperature constant is the difference $E - q$. If now the

temperature be lowered to $T - dT$, and the direction of the current reversed while unit quantity of electricity is passed, the E.M.F. and hence the electrical energy absorbed, will be $E - dE$, while the heat value of the chemical reaction will be $q - dq$. Returning the cell to its original temperature, it will also be in its original state electrically and chemically, while the residue of electrical work done by it is dE . The efficiency of the cell as a heat engine must be

$$\frac{dE}{E - q} = \frac{dT}{T},$$

whose solution is

$$E = q + T \frac{dE}{dT}.$$

In most reversible cells the first term, the heat energy of the chemical reactions, is the most important, but the complete theory has been conclusively verified experimentally by Jahn¹ and others.

Nernst² has developed a theory which relates the phenomena of the voltaic cell to those of osmotic pressure. If two portions of the same solvent are brought into contact with each other, one portion containing a given electrolyte in solution, the other not containing it, diffusion will begin to take place immediately. Now as a rule the two ions of an electrolyte do not have the same mobility, and hence will not be able to diffuse

¹ *Wied. Ann.*, 28, pp. 21 and 491, 1886.

² *Ztschr. phys. Chem.*, 4, 129, 1889. "Theoretical Chemistry," pp. 607-616.

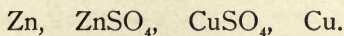
into the new space at the same rate, but the more mobile one will be present in greater numbers in the region of less concentration, giving it an electrification of its own sign, while the region of greater concentration will have an excess of the less mobile ions, and a charge of the corresponding sign. The result will be a difference of potential, which may be made available as an electromotive force in a so-called concentration cell. This electromotive force then appears immediately as a phenomenon of the varying osmotic pressures of the two ions in the different parts of the solution.

Whenever any soluble material is in contact with its solvent, its tendency to go into solution can be stated in terms of its *solution pressure*, this quantity being analogous to osmotic pressure, and measured in the same units, so that the substance dissolves, is in equilibrium, or is precipitated from the solution, according as the osmotic pressure is less than, equal to, or greater than this solution pressure. This conception can be applied equally well to simple solution of inert substances, or to the solution of a metallic electrode, whose atoms pass into the liquid as positively charged ions. When a metal is immersed in a solvent which is not saturated with its ions, there is immediately a rush of these ions into the solution; then the solution pressure of the metal may be held in equilibrium by the opposing electrostatic field, due to the positive charges of the ions and the resulting equal negative charge of the metal, as in the case of silver dipped

into a solution of salt, NaCl, or copper in dilute sulphuric acid; if the solution pressure is sufficiently high, the electric forces developed may be so great as to drive out of the solution other positive ions, as when iron is dipped into copper sulphate solution, and copper is precipitated upon the iron in quantity equivalent, electrically, to the iron dissolved.

An illustration showing the harmony of the two methods of discussions is the copper sulphate concentration cell. Suppose two copper electrodes dipping one into a region of low, the other into a region of high concentration. Then about the former there is less osmotic pressure of copper ions, hence more tendency for the copper to go into solution, resulting in a current, if the external circuit be completed, which within the liquid will pass from the less concentrated to the more concentrated portion of the cell. This will increase the concentration of the positive copper ions in the region of less concentration, and lessen it about the other electrode. The more rapid diffusion of the negative sulphion ions into the region of less concentration tends to favor the current in the same direction, so that the net result within the cell is a tendency to uniformity of concentration, by diffusion, by migration of sulphion ions, and by the passing of copper ions into or out of the solution at the electrodes.

Cells of the Daniell type are of especial interest. They may be represented by the symbols



The solution pressure of Zn is much greater than that of Cu, so that when the external circuit is closed more Zn ions pass into the solution while an equal number of Cu ions pass out onto the copper electrode, with a corresponding current having the direction from zinc to copper within the cell. It readily appears that the effect of diluting the solution of zinc sulphate about the zinc is to increase the ease with which the zinc goes into solution, and hence the E.M.F. of the cell, while diluting the copper sulphate solution for the same reason will lower the E.M.F.

The analogy between vaporization and solution makes it possible to give exact mathematical form to this theory. If the osmotic pressure follows Boyle's law, then the energy of the isothermal transformation from the osmotic pressure p to the solution pressure P of the metal, that is, the energy available from the solution of the metal, and hence the difference of potential between metal and electrolyte is

$$e = RT \log \frac{P}{p},$$

and neglecting the difference of potential between the two solutions, the E.M.F. of the Daniell cell amounts to

$$E = RT \left(\log \frac{P_1}{p_1} - \log \frac{P_2}{p_2} \right),$$

where the subscript 1 refers to zinc, and 2 to copper. This result implies that the E.M.F. of the cell is

dependent only upon the cation, and not upon the anion. This is found to be substantially true in the case of solutions which are of the same concentration and ionization, unless, as in the case of the NO_3 ion, there is action between the electrode and the solution not considered in the deduction.

This theory enables us to localize the E.M.F. of the battery cell, as existing mainly between the electrodes and the surrounding solution, and from measurements of the potentials there developed to compute the solution pressure, P for the various metals. These range¹ from 10^{44} atmospheres for magnesium and 10^{18} for zinc to 10^{-20} for copper. These solution pressures seem to be constants, dependent upon the solvent, as well as the metal, and upon the temperature, but independent, in general, of the anion.

In the irreversible type of cell the anode and its phenomena are similar to those of the reversible type of cell, but the cation which would otherwise be set free at the cathode is either absorbed by a block of carbon or oxidized; in the former case the E.M.F. is considerably reduced, the cell is said to be polarized; in the latter the oxidation furnishes a considerable supply of energy, and often cations of a different character, usually materially increasing the E.M.F. of the cell, which is, however, usually very inconstant.

The phenomena of electrolytic dissociation are confined to solutions in a very limited number of solvents, and are altogether most noticeable in water solutions.

¹ Nernst, "Theoretical Chemistry," p. 410.

These solvents are all anomalous in other respects, giving evidence of molecular complexity, and exhibiting very unusually high dielectric constants, that of water being the very highest. Attention has been called by J. J. Thomson¹ and Nernst² to the influence which the dielectric constant must have upon the electric forces existing between the ions, these forces being inversely as the dielectric constant; so that in a solvent having a very large dielectric constant the separation into ions is opposed by much smaller electrical forces. The high degree of polymerization of these solvents may be a cause of their high dielectric constants. No satisfactory quantitative relation has yet been discovered between the dielectric constants of the different solvents and their ionizing power, although the following statement will illustrate the qualitative relation:

Water, dielectric constant about 80, ionizing power greatest.

Formic acid, dielectric constant 62, ionizing power about three fourths that of water.

Methyl alcohol, dielectric constant about 33, ionizing power from one half to two thirds that of water.

Ethyl alcohol, dielectric constant about 26, ionizing power from one fourth to one third that of water.

While water is the strongest dissociating solvent, its own tendency is toward polymerization rather than dissociation, and conductivity measurements have shown

¹ *Phil. Mag.* (5), 36, p. 320, 1893.

² *Ztschr. phys. Chem.*, 13, p. 531, 1894.

so marked a dependence of that conducting power upon the presence of impurities that some have been ready to declare that *pure* water is an absolute non-conductor. The evidence seems to indicate that water itself is actually, though only very slightly, dissociated. Determinations by different methods give concordant results,¹ the concentration C_0 of the ions in gram-ions per liter being at 25° C.:

By conductivity $C_0 = .6 \times 10^{-6}$ (Kohlrausch).

By electromotive force $C_0 = 1.0 \times 10^{-7}$ (Ostwald).

By hydrolysis $C_0 = 1.1 \times 10^{-7}$ (Arrhenius-Shields).

By saponification $C_0 = 1.2 \times 10^{-7}$ (Wijs).

Kohlrausch and Heydweiller (1894) give

$$C_0 = .3373 \times 10^{-7} \text{ at } 18^\circ.$$

While there are some gaps in the theory of electrolytic dissociation, and some discrepancies to be explained, a sane review of the facts in evidence seems to indicate that the main points of the theory are well established, and the discrepancies are such as to lead to the development rather than the overthrow of the doctrine.²

Ionization of Gases. — The application of a sufficient potential-difference will cause an electric spark to pass

¹ Nernst, "Theoretical Chemistry," p. 662.

² See Wetham, *Phil. Mag.* (6), 5, pp. 279-290, 1903.

between conducting terminals in air, while the passage of the current can be maintained, once started, by a much smaller potential. The passage of the current is much easier through the moderately rarefied air of a Geissler tube, and in the high vacuum of a Crookes tube assumes quite a different character, the glow proceeding in straight lines from the cathode regardless of the position of the anode. It further appears that flames or even heated gases show considerable conducting power, that rarefied gases through which an electric discharge is passing are excellent conductors of currents due to small potentials also, as in the Zehnder tube¹ for the detection of electric waves; and that air exposed to ultra-violet light, to Roentgen rays, or the radiations from radium salts and other radioactive substances has lost its insulating properties and acquired a considerable conducting power. To explain these facts one of the theories early advanced was that of an electrolytic dissociation² of the gas; the greatest development has come with the study of the effects of radiation. J. J. Thomson and Rutherford³ have shown that air which has been exposed to Roentgen rays exhibits a behavior entirely analogous to that of a very dilute electrolyte. In their apparatus, air after being subjected to the radiation was caused to pass through an earth-connected metal tube, in whose axis is placed

¹ *Wied. Ann.*, 47, pp. 77-92, 1892.

² Giese, *Wied. Ann.*, 17, p. 538, 1882, etc. Schuster, *Proc. Roy. Soc.*, p. 317, 1884. Elster and Geitel, *Wied. Ann.*, 37, p. 324, 1889.

³ *Phil. Mag.* (5), 42, pp. 392-407, 1896.

a wire charged to a high potential. They found that with a steady stream of gas passing through the tube, an increase of potential produced a corresponding increase in the leakage-current only up to a certain limit, when the current became "saturated." The explanation is that the current depends both upon the potential and upon the supply of ions available, so that if the supply is very limited, the maximum current is that which will just exhaust the supply of ions. This view is enforced both by the fact that the air thus exhausted is no longer a conductor and by the other fact that when the leakage takes place between parallel plates, if the potential is high enough to saturate the current, the current increases continually with increase of the distance between the plates, the latter ranging in the experiments reported from .1 to 8 mm., this apparent violation of Ohm's law being due to the increase in the number of ions available for the conduction of the current; but with smaller potential difference, the current at first increased, then decreased as the distance became greater between the electrodes.

It is possible that the hot gases from flames which have been fed with suitable salts contain ions similar to those present in aqueous solution, which may furnish the mechanism for the conduction of the electric current, and may also be concerned in giving the characteristic spectrum of the vapor. But in many cases the ions concerned are of a different type, called by J. J. Thomson corpuscles,¹ which seem to be smaller than

¹ *Phil. Mag.* (5), 44, p. 311, 1897.

ordinary atoms, and of a nature independent of the source from which they are derived; so that the cathode rays seem to be a stream of negatively charged corpuscles, driven off by electrostatic repulsion, moving in straight lines unless deflected by a magnetic or an electrostatic field, and causing phosphorescence wherever it strikes the glass.

The velocity of these corpuscles was found to be, in Thomson's experiments, of the order of 10^9 cm. per sec., depending upon the difference of potential between the electrodes, as compared with 10^5 for ordinary gas molecules, while the mean effective velocity under unit potential-gradient of the ions in air which has been exposed to Roentgen radiation, as measured by the conducting power, is 1.6 cm. per sec.,¹ or for hydrogen 5.2 cm., as compared with .003 cm. per sec. for the hydrogen ion in aqueous solution.

The ratio of the mass of the ion to the charge which it carries is, in the case of the electrolysis of liquids, the common electrochemical equivalent. This ratio has been determined by Thomson in the case of the cathode rays from a study of their deviation by a magnetic or electrostatic field, since the curvature of the path depends upon the balance between the "centrifugal force," due to their inertia and velocity, and the deviating force, dependent in the electrostatic field on the charges, in the magnetic, both on charge and velocity. He finds that this ratio² is very nearly 10^{-7}

¹ *Phil. Mag.* (5), 44, p. 434, 1897.

² *Phil. Mag.* (5), 44, p. 310, 1897.

as compared with the smallest previous known value, 10^{-4} , for the hydrogen ion (expressed in the same units).

Later work indicates¹ that the charges carried by these corpuscles are of the same magnitude as those carried by ions in liquids, so that the corpuscles themselves are shown to be exceedingly small in comparison with ordinary molecules and atoms. This determination was made possible by the discovery of C. T. R. Wilson² that dust-free moist air, which has been ionized by Roentgen radiation, will produce a cloud on being subjected to an expansion which would not produce the cloud in un-ionized air. The air in question was kept saturated with moisture, and the expansion was of a measured amount, so that the quantity of water condensed could be computed, while the rate at which the cloud settled through the air enabled the computation of the size of the individual drops, and hence their number. The fact that these corpuscles, though vastly smaller than the smallest atoms, can serve as nuclei for this condensation, a function ordinarily performed only by solid dust particles, is explained by the statement³ that on a charged sphere of less than a certain radius, the effect of the charge in promoting condensation will more than counterbalance the effect of surface tension in preventing it. As a consequence, these charged ions, in spite of their diminu-

¹ *Phil. Mag.* (5), 46, p. 544, 1898; (6), 5, p. 354, 1903.

² *Phil. Trans. A.*, 1897, p. 265.

³ J. J. Thomson, "Applications of Dynamics to Physics and Chemistry," p. 164.

tive size, collect minute drops of water which act as centers of condensation.

It appears then that these corpuscles are very minute objects, so small that it takes hundreds or thousands of them to make ordinary atoms, but carrying unit ionic charges (usually negative). Being so small, their collisions with molecules must be regarded as really collisions with the corpuscles constituting these molecules, so the number of collisions of a single corpuscle and hence its free path, depends upon the total number of corpuscles present, including those in the molecules, and hence simply upon the density of the gas, and not on its material (as corpuscles from all different sources are indistinguishable in their properties).

These corpuscles are undoubtedly present to some extent in any gas,¹ being formed and destroyed by recombination continuously. When a region containing such gas is subjected to a very strong electric field, these corpuscles are given very high velocities in the direction of the field, so high that striking against gas atoms they are able to dissociate or ionize them, thus increasing the number of such carriers, so that they are adequate for the conveyance of a considerable current. This seems to be the beginning of the passage of an electric spark. The ionization by collisions can begin only when the field is strong enough to give the ions an energy or velocity which exceeds a certain critical value, sufficient to ionize a molecule by collision, and reaches its limit when the conductivity is so great

¹*Phil. Mag.* (5), 50, pp. 278-283, 1900.

as to reduce the strength of the field to or below this limit. But the energy given to a corpuscle of charge e by a field of strength F in traveling the distance l , its mean free path, is evidently measured by the product Fel , so that the field F required to produce a spark varies inversely as l , and hence directly as the density of the gas, a result which we know to be approximately true. We can see also why there might be great difficulty in securing a discharge between electrodes so near that the existing ions would have very little opportunity for hitting and ionizing the gas molecules.

Corpuscles are thus produced in considerable numbers by the collisions of previously existing corpuscles acting in a strong electric field; they are also produced by the action of certain "radiations," some of which, as the Roentgen rays and ultra-violet light, seem to be phenomena of the ether, others, as the cathode and Becquerel rays, seem to be streams of corpuscles, while the radiations from other substances seem to consist of both types. They are also given off by heated bodies, which suggests to J. J. Thomson¹ a possible explanation of some of the phenomena of the solar corona, and of comets.

The corpuscles disappear from a gas either by spontaneous recombination, in which case the number present is determined by the balance between this process and the process of generation, whether spontaneous or due to radiation; or by being carried out by the proc-

¹*Phil. Mag.* (6), 4, pp. 253-262, 1902.

ess of electrolytic convection and discharge, as in the experiments on the conductivity of gases.

In some experiments as in the "electric wind" from a highly charged point¹ or in the electrolysis of salt flames² there is room for question as to the mass of the carriers. In the former case it is suggested that the corpuscle may carry with it a cluster of molecules electrically attracted; in the latter there is room for question whether the carriers correspond to the ions active in the electrolysis of solutions or whether they consist of negatively charged corpuscles and positively charged residua, molecules which have lost one charged corpuscle.

This raises the general question whether the character of all ions may not be due to an excess or deficiency in these electrified corpuscles, anions being characterized by an excess of one or more corpuscles, cations by the corresponding deficiency.

¹ *Phil. Mag.* (5), 48, pp. 401-420, 1899.

² *Phil. Mag.* (6), 4, pp. 207-214, 1902.

CHAPTER XII.

SUMMARY.

THE aim of this work as announced in the introduction has been statement rather than discussion. In general the attempt has been to follow along lines which are tried and safe, and to present what is sometimes termed the "orthodox" treatment. As regards method of treatment, a middle course has been adopted; while there has been a free use of the notation and methods of the differential and integral calculus, in the attempt to give a presentation which should be sufficiently concrete and tangible to be grasped by students in college such abstractions as Clausius' "Virial theorem" have been avoided in spite of their great value and power. On the other hand, in the frank recognition of the ideal character of the system under construction numerical details with regard to molecules and their phenomena have been postponed to this chapter.

Many portions of the theory are still in process of construction, many points are still debatable. Maxwell's distribution of velocities has both its defenders and adversaries. According to this law the relative number of molecules having the components of its velocity u , v , and w , is dependent upon the function

$$e^{\frac{u^2 + v^2 + w^2}{\alpha^2}}.$$

The question is asked whether such a function possesses the character of permanency. Much of the work of such masters as Burbury and Boltzmann is a discussion of this fundamental point, the latter defending the law, on the assumption of the utter lack of systematic relation between the motions of the different molecules ("molekular-ungeordnet" is his phrase), while the former insists that this distribution has only a quasi-stability, complete stability being given by a distribution such that the exponent of e shall be a complete quadratic function, involving the cross-products, uv , vw , wu , with suitable coefficients. Many papers by other writers also are taken up with the intricacies of this problem.

Boltzmann's defense of Maxwell's distribution of velocities involves his famous H theorem.¹ He defines a function H , such that for a single gas, if the number of molecules having the components of their velocities between u , v , w , and $u + du$, $v + dv$, $w + dw$, be called $f du dv dw$ ²

$$H = \iiint f \log f du dv dw,$$

and the criterion of the stability of the system is that H , which can only decrease by any results of collisions, shall be a minimum and hence constant. He finds

¹ "Gasttheorie," I., pp. 32-61.

² Notice that what is here called f corresponds to the expression $nf(u)f(v)f(w)$ in Chapter II., p. 20.

this condition satisfied by Maxwell's distribution for which

$$f = \frac{n}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{u^2+v^2+w^2}{\alpha^2}} = \frac{n}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{c^2}{\alpha^2}},$$

and hence

$$\log f = \log \frac{n}{\alpha^3 \pi^{\frac{3}{2}}} - \frac{c^2}{\alpha^2},$$

so that

$$H = \log \frac{n}{\alpha^3 \pi^{\frac{3}{2}}} \int \int \int f du dv dw - \frac{1}{\alpha^2} \int \int \int f c^2 du dv dw$$

but the value of the first integral is n , and of the second $n\bar{c}^2$, while $\bar{c}^2/\alpha^2 = \frac{3}{2}$, so that

$$H = n \left(\log \frac{n}{\alpha^3 \pi^{\frac{3}{2}}} - \frac{3}{2} \right).$$

But since $\bar{c}^2/\alpha^2 = \frac{3}{2}$, $\frac{1}{3} N m \bar{c}^2 = RT$ and $n = N/v$,

$$\alpha = \sqrt{\frac{2RT}{Nm}},$$

$$\begin{aligned} H &= n \left(\log \frac{N^{\frac{5}{2}} m^{\frac{3}{2}}}{v \pi^{\frac{3}{2}} 2^{\frac{3}{2}} R^{\frac{3}{2}} T^{\frac{3}{2}}} - \frac{3}{2} \right), \\ &= n \log (v^{-1} T^{-\frac{3}{2}}) + \text{Const.} \end{aligned}$$

But on p. 52 we have shown that for an ideal gas the entropy is

$$\begin{aligned} S &= C_v \log T + R \log v + \text{Const.}, \\ (22) \quad &= R \log (v T^{\frac{C_v}{R}}) + \text{Const.}, \end{aligned}$$

or for a monatomic gas, for which $C_v/R = \frac{3}{2}$,

$$S = R \log (v T^{\frac{3}{2}}) + \text{Const.}$$

So that but for the arbitrary constant term the, entropy appears as a negative multiple of H , and hence intimately connected with the stability of the distribution of velocities, and with the impossibility of individual treatment of the molecules. In this connection it is worthy of note that the entropy was defined by the equation

$$dS = \frac{dQ}{T}$$

in which $1/T$ was an integrating factor, so that S was a function or property depending only on the state of the body, and the equation

$$\oint \frac{dQ}{T} = 0,$$

which expresses that fact is also the mathematical expression of the second law of thermo-dynamics, which again seems to depend upon our inability to deal individually with molecules; both methods of discussion then seem to point to a relation between entropy and the character of the molecular motions.

Another bone of contention is the doctrine of degrees of freedom, stated on p. 75. The treatment there given yields approximate values of the ratio of the two specific heats, and we have shown (pp. 134-135) that the variation between the behavior of actual and ideal gases would introduce a slight corrective factor, the

computed correction being of the same order as the observed variations.¹ But the motions there considered, of translation and rotation, are not the only motions conceivable or probable to a molecule. We can add relative displacements of the atoms, and atomic disturbances, both of which would be oscillatory, periodic motions. We have then the peculiar fact that in counting degrees of freedom to ascertain the distribution of energy, in investigating specific heats, motions of translation and rotation are to be considered, but not motions of vibration; that is, the two former classes of motions are so intimately related that in the whole body of gas the kinetic energy tends to distribute itself as uniformly among all their degrees of freedom as between the three chosen components of the translational motion; but the vibrational motions seem to be linked, not with these other motions but with the ether, and to attain their equilibrium mainly through the process of radiation. Jeans² has shown that the period of such vibrations is so small in comparison with the probable time of a collision that the collisions between molecules will not tend, on the whole, to produce vibrations sufficient to take up any considerable proportion of the energy; but the "corpuscles," with their very much lesser size and higher speed will be able to produce such vibrations. This would suggest that radiation from gases, including luminosity, is largely conditioned upon the presence of

¹ *Phys. Rev.*, XII., pp. 353-358, 1901.

² *Phil. Mag.* (6), pp. 279-286, 1903.

considerable numbers of these corpuscles, the high temperature increasing the vigor of their attacks, and the readiness of their formation.

Another question of interest is the escape of gases from our atmosphere. A rough computation shows that an object falling from an infinite distance to the surface of the earth ought to attain a speed of about one million cm. per sec. We found (p. 14) that the average speed of the hydrogen molecule at ordinary temperatures was a little less than two hundred thousand cm. per sec., that is, a little less than a fifth of this value. At the "free surface of the atmosphere," if we were to regard such as existing, a speed not much less than the million cm. per sec. would be necessary for the escape of the molecule from the range of the earth's attraction, while the lower temperature would probably lessen the actual speeds as much or more relatively than the greater distance from the earth would lessen the speed necessary for escape. The figures given on p. 31 would indicate that for so light a gas as hydrogen less than one molecule in 10^{10} would have sufficient speed to escape, while the heavier gases of the atmosphere, having speeds about one fourth as great, would have an inconceivably small chance for escape. Any considerable loss then must be confined to the lighter gases, and while they escape with considerable rapidity from the immediate neighborhood of the earth's surface, by diffusion and convection, it is problematical whether they escape absolutely from the earth's atmosphere to any great extent.

In the development of the theory of ideal gases it was definitely assumed that no forces acted except during that portion of the experience of a molecule which was termed a collision, and no assumption was made regarding the forces there developed except that the restitutional elasticity was perfect, so that no energy was lost in the collisions. In the later development of van der Waals' equation, while the presence of attractive forces was granted, no assumption was made, apparently at least, further than that the forces acting in gases were of the same nature as those producing surface tension in liquids.

The question arises whether the forces resulting in cohesion and capillarity are the same as the ordinary gravitational attraction. The simplest analytic treatment of capillarity is to regard the liquid as a homogeneous medium, compute the mutual energy of two different elements, and integrate over the whole volume. Gauss, van der Waals and others have found for the potential energy of the liquid state an expression of the form $-A\rho$ where ρ is the density and A a constant depending upon the particular liquid and the temperature. Working backwards to the law of the force between the individual elements, it has appeared not to be of the simple gravitational type. One explanation offered is that the force is really such as to be expressed by a mathematical function of such form that for finite distances it has the common Newtonian form. Bakker¹ has suggested for the potential func-

¹ *Drude's Annalen* (4), 11, pp. 207-217, 1903.

tion of this force, instead of the form A/r , the more complicated

$$\frac{A(r + \sigma)}{r^2} e^{\frac{\lambda}{r + \sigma}},$$

in which λ is a distance varying inversely as the temperature, of such an order that at finite distances the function becomes Newtonian. Another analytical expression for the force would be a series of the form

$$\frac{a}{r^2} + \frac{b}{r^3} + \frac{c}{r^4} + \dots,$$

where all the coefficients after the first are so small that for finite distances the terms drop out, giving their effect only at molecular distances. Many have suggested that the molecular forces vary as the inverse fourth power of the distance. This relation may be deduced in rather arbitrary fashion from van der Waals' equation as follows :

Clausius' virial equation may be written¹

$$\Sigma \frac{1}{2} mc^2 = \frac{1}{2} \Sigma F \cdot r + \frac{3}{2} pv,$$

or for a single gas

$$pv = \frac{1}{3} Nmc^2 - \frac{1}{3} \Sigma F \cdot r,$$

where F represents the force acting between two molecules, and r their distance apart, the summation being

¹ van der Waals, "Continuität" (2d ed.), I., p. 8, eq. (9).

taken so as to include N molecules. Changing the first member to read $p(v - b)$, and comparing with van der Waals' equation,

$$\frac{a}{v^2}(v - b) = \frac{1}{3}\Sigma F \cdot r,$$

or disregarding b as small

$$\frac{a}{v} = \frac{1}{3}\Sigma F \cdot r.$$

If now

$$F = \frac{k}{r^h}, \quad Fr = \frac{k}{r^{h-1}},$$

$$\frac{a}{v} = \frac{1}{3}\Sigma \frac{k}{r^{h-1}}.$$

But the values of r are evidently proportional to $\sqrt[3]{v}$, and hence v is proportional to r^3 , and

$$h - 1 = 3,$$

$$h = 4;$$

hence the correction term in van der Waals' equation would seem to suggest an attraction between the molecules, varying inversely as the fourth power of the distance.

Similarly Boltzmann¹ has developed some parts of the theory on the assumption that the phenomena of

¹ "Gastheorie," I., III. Abschnitt, pp. 153-204.

collision are due to a repulsive force between the molecules proportional to the fifth power of the distance.

But to state the mathematical law of inter-molecular forces only tells *how* they act, not *why*. It has been suggested by many thinkers that these forces may be, in part at least, electrical. This suggestion is especially pertinent on account of the recent vigorous development of the theory of electrolytic dissociation and the related theory of electrons. Thus it is suggested that the electrical forces between ions, which have electric charges of one sign, are proportional to the inverse square of the distance, while the forces between neutral molecules, which are supposed to have their charges not neutralized but located at two near points within the molecule, like the forces between other electrical and magnetic doublets, must vary as the inverse fourth power. This difference in the character of the force is mentioned¹ as a possible explanation of discrepancies between results of conductivity determinations and freezing- and boiling-point methods with electrolytic solutions.

In Chapter IV. we have developed the formula for the viscosity of a gas

$$(28) \quad \eta = \frac{1}{3} nm\bar{c}l.$$

The coefficient of viscosity, η , can be determined by experiment, hence we can find the mean free path, l , which is, writing for nm its value ρ , the density of the gas,

¹ Wetham, *Phil. Mag.* (6), 5, p. 285, 1903.

$$l = \frac{3\eta}{\rho\bar{c}}.$$

The number of collisions per second of a single molecule is

$$P = l/\bar{c}.$$

The following results are taken from Ö. E. Meyer:¹

	η	l	P
Hydrogen,	.000093	.00001855 cm.	9.48 · 10 ⁶
Nitrogen,	184	936 "	4.76 "
Oxygen,	212	1059 "	4.07 "
Carbon monoxide,	184	985 "	4.78 "
Carbon dioxide,	160	680 "	5.51 "
Chlorine,	141	474 "	6.24 "
Steam,	975	649 "	9.04 "

Many different methods have been employed for finding the dimensions of the molecules. In the formula

$$(24) \quad l = \frac{3}{4\pi n\sigma^2}$$

$\pi\sigma^2$ is evidently four times the cross-sectional area of one molecule, and $n\pi\sigma^2$ that of all the molecules in a cubic centimeter of gas, so the $n\pi\sigma^2/4 = 3/16l$ would be approximately the area covered by the molecules if arranged in close order in a single layer. For the substances in the preceding table these areas range from 9,500 for hydrogen to 37,300 for chlorine, that is, from one to four square meters, approximately. But we

¹"Gastheorie" (edition 1877), quoted in Winkelmann's "Handbuch," II., 2, p. 581.

have shown in Chapter VIII., p. 179, that the minimum volume which could be attained by N spherical molecules was

$$b_1 = \frac{1}{2} \sqrt{2} N \sigma^3.$$

Applying this result to n molecules of gas, using the other value of the mean free path

$$(25) \quad l = \frac{1}{\sqrt{2} \pi n \sigma^2},$$

and multiplying

$$b_1 l = \frac{\sigma}{2\pi},$$

$$\sigma = 2\pi b_1 l.$$

The other formula for l , combined with the value $n\pi\sigma^3/6$, the volume of the n spheres, gives the slightly larger value often quoted

$$\sigma = 8b_1 l.$$

Now b_1 , the least possible volume occupied by what was originally one cubic centimeter of gas under atmospheric pressure, as a result of the greatest pressure which can be applied, cannot be very much less than the volume in the liquid state. On the assumption that they are the same, Meyer gives the following results, computed from the last formula :

	b_1	σ
Water,	.00081	$44 \cdot 10^{-9}$ cm.
Carbon dioxide,	198	114 " "
Chlorine,	238	96 " "

Again, in deducing van der Waals' equation, we found (p. 70),

$$\frac{b}{v} = \frac{1}{2} \frac{\sigma}{l}$$

from which

$$\sigma = 2 \frac{bl}{v},$$

which gives the following results :¹

	b/v	σ
Air,	.00387	$56 \cdot 10^{-9}$ cm.
Nitrogen,	232	34 " "
Carbon dioxide,	78	8 " "
Hydrogen,	318	88 " "

While neither of these methods could be expected to give a high degree of accuracy, and the first particularly ought to give results too large, their evidence as to the order of magnitude is of considerable value. Other independent methods quoted by Jaeger give molecular diameters of the same order, ranging from 9×10^{-9} to 70×10^{-9} .

Corroborative evidence is furnished by measurements of the thickness of the thinnest films which are able to produce certain effects. Thus Quincke found that a film of silver of the thickness 5×10^{-6} cm. affected the the adhesion between water and a glass plate. Parks² has detected films of water condensed on the surface of glass, ranging from 7×10^{-6} to 13×10^{-6} cm. in thickness. Johonnott³ has measured the thickness of the

¹ Jaeger, in Winkelmann's "Handbuch der Physik," II., 2, p. 601.

² *Phil. Mag.* (6), 5, p. 518, 1903.

³ *Phil. Mag.* (5), 47, p. 522, 1899.

“black spot” in a soap-film, supposed to be twice the range of molecular attraction. He found two definite thicknesses, that of the “first black spot” being 11.2×10^{-7} cm., of the “second black spot” about half as great, 6.2×10^{-7} . These results are of considerable value as giving a large upper limit.

Lord Kelvin¹ has given a review of the data and some valuable conclusions. He says: “It is scarcely conceivable that there can be any falling off in the contractile force” of a water film “so long as there are several molecules in the thickness,” and that consequently there are not several molecules in a thickness of 10^{-5} cm. He quotes the work of Rayleigh and Roentgen on thin films of oil on the surface of clean water. The former found the motion of bits of camphor affected by a film 10.6×10^{-8} cm. thick, but not by one of 8.1×10^{-8} cm. The latter, using ether, was able to detect a film 5.6×10^{-8} cm. thick. Rayleigh himself suggests that these thin films probably contain “merely molecules of oil lying at greater and less distances from one another, but at no part of the film one molecule of oil lying above another or resting on others.”

Kelvin² gives a discussion somewhat similar to that just given. From data on viscosity he finds the value of $n\sigma^2$; assuming that the molecules are arranged in the liquid state in cubic order with distances $q\sigma$ from center to center, q being simply a ratio, the volume

¹*Phil. Mag.* (6), 4, pp. 177 and 281, 1902.

²*Loc. cit.*, p. 196.

occupied by n molecules is $n(q\sigma)^3$. Argon, being monatomic, seems to approach more nearly the ideal conditions assumed in our deductions, of hard round molecules, and hence seems the most suitable of those gases for which sufficient data are available for testing the theory. He gives the following numerical results :

$$n(q\sigma)^3 = 1/681,$$

$$n\sigma^2 = 57700,$$

$$n = 681^2 \cdot 57700^3 q^6 = 8.9 \cdot 10^{19} q^6,$$

from which he concludes, since q is likely to be slightly greater rather than less than unity, to give reasonable mobility to the liquid, that a fair value for n is 10^{20} . This value is just about five times as large as that frequently quoted, $21 \cdot 10^{18}$.

On the assumption of this value of n , he gives the following data :

Gas.	ρ	\bar{c}	$n\sigma^2$	σ	m	l
CO ₂	.001974	39,200	89,500	2.99 · 10 ⁻⁸	19.74 · 10 ⁻²⁴	2.52 · 10 ⁻⁶
H ₂	.000090	184,200	32,900	1.81 "	0.90 "	6.84 "
CO	.001234	49,600	61,300	2.48 "	12.34 "	3.62 "
N ₂	.001257	49,000	61,600	2.48 "	12.57 "	3.64 "
O ₂	.001430	46,100	57,500	2.40 "	14.30 "	3.91 "
Argon	.001781	41,400	57,700	2.40 "	17.81 "	3.89 "

It will be seen that these later values of the diameters of molecules are of the same order as those found by the older workers.

J. J. Thomson,¹ using air ionized by the radiations from radium, counting the number of corpuscles by

¹ *Phil. Mag.* (6), 5, p. 354, 1903.

the rate of fall of the cloud of moisture precipitated upon them by a suitable expansion, finds the mean value of the ionic charge to be $3.4 \cdot 10^{-10}$ electrostatic units. H. A. Wilson¹ using air ionized by Roentgen rays finds the very similar value $3.1 \cdot 10^{-10}$. Granting that the charge on an ion produced by radiation is equal to that on the hydrogen ion or atom in solutions, as shown by Townsend,² these results give, approximately

$$n = 4 \cdot 10^{19}$$

about two fifths of the value of n as found by Kelvin.

In the last chapter the work of Thomson was quoted showing that the ratio of the mass to the charge of the gaseous ion was about 10^{-7} (in electromagnetic units) while for the hydrogen ion in solution it is about 10^{-4} , so that the mass of a corpuscle is of the order 10^{-3} as compared with that of the hydrogen atom, and its dimensions of the order of $1/10$, if the corpuscles making up the atom are in close array. Using Kelvin's values for the hydrogen molecule (two atoms) the mass of the corpuscle would be of the order of $5 \cdot 10^{-28}$, σ about 10^{-9} , \bar{c} about $8 \cdot 10^6$ cm. per sec., and the mean free path in hydrogen at 0° and 76 cm. pressure about 10^{-6} cm., \bar{c} thus being larger, and l smaller than for the molecules of the gases.

¹ *Phil. Mag.* (6), 5, p. 440, 1903.

² *Phil. Trans.*, A, p. 129, 1899.

INDEX.

- Absorption of gases, 189
 Acids, strong, 241, 249
 Action, spheres of, 58
 Activity, chemical, related to ionization, 249 ; coefficient of, 239, 244
 Adiabatic, 47 ; equation of, 49 ; expansion of saturated vapor, 115 ; for substance following van der Waals' equation, 132
 Amagat, experiments on high pressures, 124
 Ammonium chloride, dissociation of, 242
 Andrews, 109
 Anion, 243
 Anode, 243
 Area of molecules, 275
 Argon, 279
 Arrangement of atoms, 76
 Arrhenius, 238
 Assumptions of elementary theory, 7
 Atmosphere, escape of gases from, 270
 Atoms, 3 ; arrangement of, 76
 Average speed, 28
 Avogadro's law, 43 ; applied to osmotic pressure, 203
b, value of, 69, 70
 Bakker, 271
 Bases, strong, 241, 249
 Bernouilli, Daniel, 1
 Berthelot, equations of, 150
 Boiling point, elevation of, 209
 Boltzmann, 1, 84, 89, 225, 266, 273 ; theorem of "degrees of freedom," 75 ; H theorem, 266
 Boyle's law, 15 ; variation from, 124 ; osmotic pressure follows, 202
 Burbury, 266
 Cailletet and Mathias, rule of, 143
 Carbon dioxide, isothermals of, 109
 Carnot's cycle, 47, 113
 Cathode, 243 ; rays, 258, 260 ; rays, deviation of, 260
 Cation, 243
 Cell, osmotic, 199 ; galvanic, theory of, 250 ; irreversible galvanic, 255
 Change of state, thermodynamics, 112
 Charge, effect of electric, on condensation of moisture, 261 ; on ions, 242, 261, 280 ; on molecules, 80
 Charles' law, 15 ; variation from, 124 ; osmotic pressure follows, 202
 Chemical activity related to ionization, 249
 Clausius, 1, 239, 265 ; equation of, 123
 Cloud, produced in ionized air, 261
 Coefficient of activity, 239, 244 ; of pressure-change, 126 ; of volume-

- change, 127 ; of viscosity, 87, 89 ; dependent upon size of molecules, 90 ; upon temperature, 91 ; variations in, 92
- Cohesive forces in fluid, 121
- Collisions, 8 ; effect on distribution of energy, 39 ; of single molecule, 56 ; number of, 59, 275 ; in mixed gas, 100 ; number causing dissociation, 227 ; producing recombination, 229 ; ionization by, 262
- Colored ions, 240
- Component velocities, 18, 33
- Compressibility of liquid, 184
- Concentration, change of, in electrolyte, 243 ; -cells, 252
- Condensation of moisture on corpuscles, 261
- Conduction of electricity, 79 ; of heat, 92
- Conductivity, electrical, 84 ; thermal, 94 ; dependent on temperature, 95 ; correction at surface, 95 ; of electrolytes, 241, 244 ; molecular, 244, 246 ; dependent on viscosity, 248 ; of gas, 259
- Constant pressure, specific heat at, 45
- Constant volume, specific heat at, 44
- Constitution of water, 237
- Continuity of liquid and vapor states, 117
- Coördinates, division of energy between, 37
- Copper, solution pressure of, 255
- Corpuscles, 259 ; production of, 262 ; mass of, 280 ; mean free path of, 280
- Correction of thermal conductivity, 95
- Corresponding states, 140
- Covolume, 152, 165 ; of liquid, 181 ; in solution and surface film, 220
- Critical data, 143 ; point, 110 ; for van der Waals' equation, 138 ; volume, ideal, 145
- Crookes' tube, 258
- Current, electric, 83
- Curve of probabilities, 23
- Cycle, Carnot's, 47, 113
- Dalton's law, 39
- Daniell cell, 253
- Data of critical state, 143
- Decomposition, double, 224
- Degrees of freedom, 75, 268
- Demon engine, Maxwell's, 54
- Density, related to pressure, 13 ; relative, of vapor and liquid, 160, 165 ; effect upon dissociation, 231 ; of dissociated gas, 236 ; effect of, on electric discharge in gases, 263
- Depression of vapor pressure, 207 ; of freezing point, 211
- Deviation of cathode rays, 260
- Diameter of molecules, 276
- Dielectric constant, related to ionizing power, 256
- Dieterici, equation of, 123, 147, 149 ; deduced, 171 ; related to equation of van der Waals, 173 ; treatment of vaporization, 154
- Diffusion of gases, 96 ; "into itself," 99 ; rate of, 103 ; simplifications, 105, 107
- Di-hydrol, 237

- Dilution, heat of, 213, 222
Discharge, electric, in gases, 258
Dissociated gas, equations for, 232 ;
density of, 236
Dissociating power of solvents, 256
Dissociation, gaseous, 224 ; by col-
lision, 226 ; into like parts, 227 ;
collisions causing, 227 ; affected
by density, 231 ; temperature of,
236 ; electrolytic, 238 ; constant,
247 ; of water, 257
Distance travelled by molecule,
64 ; between molecules in liquid,
175, 178, 180, 278
Distillation, 198
Distribution of velocities, 18, 266 ;
of speeds, 25, 154, 164 ; of
energy after collision, 39
Divisibility of matter, 2
Division of energy among coördi-
nates, 37
Double decomposition, 224
Doublets, 274
Efficiency of cycle, 114
Electrical conductivity, 84, 241
Electric charge on ion, 242 ; effect
on condensation of moisture, 261 ;
current, 83 ; discharge in gases,
258, 262 ; spark, 262 ; wind,
264
Electrical forces, 274
Electricity, conduction of, 79
Electro-chemical equivalent, 260
Electrodes, 243
Electrolyte, change of concentra-
tion, 243 ; conductivity of, 241,
244
Electrolytes, specific gravities of,
240
Electrolytic dissociation, 238
Elevation of boiling point, 209
E.M.F. of galvanic cell, 251, 254
Energy, division among coördi-
nates, 37 ; distribution after col-
lision, 39 ; intrinsic, 44 ; inde-
pendent of volume, 44 ; of
translation, 73 ; total, 73 ; car-
ried by molecules passing into
vapor, 158 ; potential, of liquid
film, 170 ; internal, 226 ; poten-
tial, of liquid, 271
Engine, Carnot's reversible, 47 ;
Maxwell's demon, 54
Entropy of ideal gas, 51, 268 ; of
saturated vapor, 116 ; of sub-
stance following van der Waals'
equation, 131 ; of mixed gas,
186
Equation of adiabatic, 49 ; of van
der Waals, 122 ; of Clausius,
123 ; of Dieterici, 123, 147,
149, 171
Equivalent, electro-chemical, 260
Escape of gases from atmosphere,
270
Exhaustion of conductivity of gas,
259
Expansion of saturated vapor, 115
Faraday's law, 242
Fifth power, inverse, 273
Film, semi-permeable, 200 ; poten-
tial energy of liquid, 170 ; thick-
ness of, 277
First law of thermodynamics, 43,
213 ; for saturated vapor, 114 ;
for substance following van der
Waals' equation, 129
Flames, conduction in, 259

- Forces between molecules, 271
 Fourth power, inverse, 272
 Fractional distillation, 198
 Freedom, degrees of, 75, 268
 Free path, mean, 55, 59, 64, 275 ;
 in liquid, 176, 180 ; of corpus-
 cles, 262, 280
 Free surface, 5
 Freezing point. depression of, 211
- Galvanic cell, 250 ; irreversible,
 255
 Gas, thermodynamics of ideal, 43 ;
 equations for ideal, 132 ; for one
 following van der Waals' equa-
 tion, 133 ; equations for disso-
 ciated, 232 ; density of disso-
 ciated, 236 ; conductivity of,
 259 ; methods of ionizing, 263
 Gases, ideal, 7 et seq. ; viscosity of,
 85 ; diffusion of, 96 ; do not fol-
 low laws of Boyle and Charles,
 120 ; mixed, 185 ; absorption of,
 189 ; ionization of, 257 ; radia-
 tion from, 269
 Gaseous dissociation, 224 ; spec-
 trum, 259
 Gauss, 271
 Gay Lussac's law, 15
 Geissler tube, 258
 Gravities, specific, of electrolytes,
 240
- H theorem, 266
 Half-electrolytes, 247
 Heat, specific, at constant volume,
 44 ; at constant pressure, 45 ; of
 molecule, 46, 71 ; of saturated
 vapor, 113 ; at constant pressure,
 130 ; of isothermal transforma-
 tion, 50 ; conduction of, 92 ;
 latent, 113, 169, 208, 210, 219 ;
 of dilution, 213, 222 ; specific
 and latent, of water, 238
 Heats, ratio of specific, 45 ; value
 of ratio, 77 ; ratio of specific, for
 substance following van der
 Waals' equation, 134 ; ratio of,
 268 ; of neutralization, 242
 Helmholtz, 250
 Henry's law, 189
 Hydrodynamica, Bernoulli's, 1
 Hydrogen, behavior of, 69 ; escape
 of, from atmosphere, 270
 Hydrol, 237
- Ice, constitution of, 237
 Ideal gas, 7 ; pressure of, 9 ;
 thermodynamics of, 43 ; equa-
 tions for, 132
 Ideal isothermal, 116
 Impact, momentum transferred
 during, 10, 33 ; at right angles,
 16 ; probability of, 56
 Impacts, number per second, 11, 33
 Impulse, summation of, 35
 Indicators, 240
 Integration, methods of, 22, 27, 30
 Internal pressure, 122, 153, 182
 Internal energy, 226
 Inverse fourth power, 272 ; fifth
 power, 273
 Ionic charge, 242, 261, 280
 Ionization, constant, 239, 244 ; of
 water, 257 ; of gases, 257 ; of
 gas, methods of, 263
 Ionizing power of solvents, 256
 Ions, 239 ; their properties addi-
 tive, 239 ; colored, 240 ; valence
 of, 243 ; migration of, 244 ;

- velocity of, 245 ; speed in air, 260 ; mass of, 280
- Isothermal, 47 ; transformation, heat and work of, 50 ; ideal, 116
- Isothermals of carbon dioxide, 109 ; form for van der Waals' equation, 135
- Irreversible galvanic cell, 255
- Iso-osmotic solutions, 202
- Jaeger, 277
- Jahn, 251
- Jeans, 269
- Johannott, 277
- Joule, 1
- Kelvin, 72, 278
- Kinetic theory of solutions, 216 ; of dissociation, 225
- Kohlrausch, 245
- Latent heat, 113, 169, 208, 210, 219
- Latent heats of water, 238
- Layer, non-homogeneous, 155, 216
- Length of path, probability of, 64
- Limited solubility, 192
- Liquid state, 4 ; film, potential energy of, 170 ; molecules within, 174 ; solutions, 189, 192 ; potential energy of, 271
- Lodge, 245
- Luminosity of gases, 269
- Magnesium, solution pressure of, 255
- Mass of ions, 264 ; of molecules, 279 ; of corpuscles, 280
- Mariotte's law, 15
- Maxwell, 1, 42 ; distribution of velocities, 21, 265 ; distribution of speeds, 25, 154, 164 ; demon engine, 54 ; deduction of relative speeds, 60 et seq.
- "Mean square" of speed, 29
- Mean free path, 55, 59, 64, 275 ; in mixed gas, 100, 103 ; in liquid, 176, 180 ; of corpuscle, 280
- Membrane, semi-permeable, 200
- Method of integration, 22, 27, 30
- Meyer, O. E., 107, 275
- Migration of ions, 244
- Milner, 169
- Minimum volume, 179, 276
- Mixed gas, mean free path in, 100, 103
- Mixed vapors, 194
- Mixture of gases, pressure of, 38
- Mixtures, 185
- Model, 111
- Molecular specific heat, 46 ; pressure, 122, 153 ; conductivity, 244, 246
- Molecule, mean kinetic energy proportional to temperature, 42
- Molecules, 3 ; oscillation of, 4 ; speed of, 14 ; number having different speeds, 30 ; number making given angle with a plane, 34 ; effect of their volume, 69 ; their potentials and charges, 80 ; number passing into vapor, 156 ; volume of, 179 : forces between, 271 ; electrical forces between, 274 ; area of, 275 ; diameter of, 276 ; mass of, 279 ; number of, 279
- Momentum transferred during im-

- pact, 10, 33; carried by molecule into vapor, 161
 Most probable speed, 26
 Motions, vibratory, 269
 Nernst, 153, 204, 241, 251, 256
 Neuclei, ions as, 261
 Neutralization, heats of, 242
 Newton's laws applicable to molecules, 3
 Newtonian potential, 271
 Non-homogeneous layer, 155; film, 216
 Noyes, 249
 Number of impacts per second, 11, 33; of molecules having different speeds, 30; of collisions, 59, 275; of collisions causing dissociation, 227; of collisions causing recombination, 229; of molecules passing into vapor, 156; of molecules, 279
 Ohm's law not followed by gas, 259
 Osmosis, 199
 Osmotic pressure, 199, 222; effect of temperature, 201, 215; related to vapor pressure, 205; thermodynamics of, 213; anomalous, 238
 Ostwald, 240, 247
 Parks, 277
 Partial pressures in solution, 218
 Path, mean free, 55, 59, 64, 275; in mixed gas, 100, 103; in liquid, 176, 180; of corpuscles, 262, 280
 Path, probability of given length, 64
 Pfeffer, 199
 Point, critical, 110; for van der Waals' equation, 138
 Polarization of galvanic cell, 255
 Potential of molecules, 80; energy of liquid film, 170; energy of liquid, 271
 Pressure of ideal gas, 9, 13; recomputed, 32; due to several gases, 38; modified by volume of molecules, 67; molecular, 122; internal, 153; -change, coefficient of, 126; of saturated vapor, by van der Waals' equation, 137; critical, 139; reduced, 140; in liquid, 180; of vapor over solution, 194; osmotic related to vapor, 205; osmotic, 222; anomalous osmotic, 238; solution, 252; partial, in solution, 218
 Probabilities, theory of, 18
 Probability curve, 23; of length of path, 64
 Probable speed, 26
 Quincke, 277
 Radiation from gases, 269
 Radiations capable of ionizing gases, 263
 Ramsey and Young, 146
 Raoult's law, 212, 223
 Ratio of two specific heats, 45, 77, 268; of mass to charge, 260
 Rayleigh, 154, 278
 Rays, cathode, 158, 260; deviation of, 260
 Reactions, chemical, influenced by presence of water, 249
 Recombination of molecules, 229

- Reduced pressure, volume and temperature, 140
- Relative speed, 60 ; in mixed gases, 102
- Repulsive forces, 273
- Reversible transformations and cycle, 47 ; galvanic cell, 250
- Roentgen, 278 ; rays, 258
- Rudolphi, 248
- Rutherford, 258
- Saturated vapor, 6 ; specific heat of, 113 ; according to van der Waals' equation, 137
- Second law of thermodynamics, 53, 268
- Semi-permeable partition, 186 ; film, 200
- Separation of mixed gases, 186 ; of solvent, 205
- Solid state, 4 ; solutions, 188
- Solubility, 249 ; of various gases, 190
- Solution of gases, 189 ; of liquids, 192 ; vapor over, 193 ; partial pressures in, 218 ; pressure, 252
- Solutions, kinetic theory of, 216
- Solvent, separation of, 205
- Solvents, ionizing power of, 256
- Space occupied by molecules, 179
- Spark, electric, 262
- Specific gravities of electrolytes, 240
- Specific heat at constant volume, 44 ; at constant pressure, 45 ; at constant pressure for substance following van der Waals' equation, 130 ; of molecule, 46 ; of saturated vapor, 113 ; of water, 238
- Specific heats, ratio of, 45, 77, 268 ; for substance following van der Waals' equation, 134
- Spectrum, gaseous, 259
- Speed of molecules, 14 ; most probable, 26 ; average, 26 ; "mean square," 29 ; relative, 60 ; of ions, 243, 245 ; of cathode rays, 260
- Speeds, distribution of, 25, 154, 164 ; number of molecules having different, 30 ; relative, in mixed gas, 102 ; in liquid and vapor, 160, 164
- Spheres of action, 58
- States, corresponding, 140
- Statistical method, 9
- Steam line, 110
- Strong acids and bases, 241, 249
- "Sugar gas," 204
- Sugar-solution, osmotic pressure of, 201
- Summation of impulses, 35
- Surface film, 155, 216 ; covolume in, 220
- Surface tension, 183, 237
- Sutherland, on constitution of water, 237
- Temperature, scale defined, 15 ; depends on mean kinetic energy of molecules, 42 ; critical, 139 ; reduced, 140 ; of dissociation, 236
- Tension, surface, 183, 237
- Thallous chloride, 249
- Theory of Probabilities, 18
- Thermal conductivity, 94 ; dependent on temperature, 95 ; correction at surface, 95
- Thermodynamics, scope, 2 ; first

- law, 43 ; of ideal gas, 43 ; second law of, 53, 268 ; of change of state, 112 ; of substance following van der Waals' equation, 128 ; of osmotic pressure, 213 ; of galvanic cell, 250
- Thin films, 277
- Thomson, Prof. James, 116
- Thomson, J. J., 256, 258, 279
- Townsend, 280
- Total energy, 73
- Transformation, defined, 47 ; work and heat of isothermal, 50
- Translation, energy of, 73
- Traube, 152
- Tri-hydrol, 237
- Tube, vacuum, 258
- Valence of ions, 243
- Valson, 240
- Values of ratio of specific heats, 77
- Van der Waals, 271 ; equation of, 122 ; thermodynamics of substance following equation of, 128 ; entropy, 131 ; equations relating to, 133 ; ratio of specific heats, 134 ; form of isothermals, 135 ; vapor pressure, 137 ; critical point, 138
- Van't Hoff, 202, 238, 248
- Vapor, saturated, 6 ; specific heat of saturated, 113 ; adiabatic expansion of saturated, 115 ; pressure according to van der Waals' equation, 137 ; pressure, reduced, 141 ; number of molecules passing into, 156 ; density, 160, 165 ; over solution, 193 ; pressure, osmotic pressure related to, 205
- Vaporization, 5, 109, 155 ; thermodynamics of, 112
- Velocities, distribution of, 266
- Velocity lines, 17 ; number, 18 ; independent of direction, 20 ; Maxwell's distribution, 21
- Velocity-function, 19
- Velocity of ions, 245
- Vibratory motions, 72, 269
- Virial, 265, 272
- Viscosity of gases, 85, 274 ; coefficient of, 87, 89
- Volume, of molecules, effect of, 69 ; -change, coefficient of, 127 ; reduced, 140 ; critical, 139, 145 ; in liquid state, 174 ; minimum, 179, 276 ; of molecules, 179
- Waals, van der, 271 ; equation of, 122 ; equations for substances following, 133 ; ratio of specific heats, 134 ; form of isothermals, 135 ; vapor pressure, 137 ; critical point, 138
- Walker, 246
- Water line, 110 ; constitution of, 237 ; specific and latent heats, 238 ; undissociated, 241 ; presence in chemical reactions, 249 ; dissociation of, 257
- Wetham, 204, 246, 257, 274
- Wilson, C. T. R., 261
- Wilson, H. A., 280
- Wind, electric, 264
- Work of isothermal transformations, 50 ; of vaporization, 167
- X-rays, 258
- Young, 141, 146
- Zehnder tube, 258
- Zinc, solution pressure of, 255

14 DAY USE
RETURN TO DESK FROM WHICH BORROWED

LOAN DEPT.

This book is due on the last date stamped below, or
on the date to which renewed.

Renewed books are subject to immediate recall.

3 Nov 64 RB

REC'D LD

NOV 3 '64-10 AM

19 Oct '65 YS

REC'D LD

OCT 5 '65-11 AM

LD 21A-40m-11,'63
(E1602s10)476B

General Library
University of California
Berkeley

RETURN TO the circulation desk of any
University of California Library
or to the

NORTHERN REGIONAL LIBRARY FACILITY
Bldg. 400, Richmond Field Station
University of California
Richmond, CA 94804-4698

ALL BOOKS MAY BE RECALLED AFTER 7 DAYS

- 2-month loans may be renewed by calling (510) 642-6753
 - 1-year loans may be recharged by bringing books to NRLF
 - Renewals and recharges may be made 4 days prior to due date.
-

DUE AS STAMPED BELOW

SEP 3 1999
